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WRDC-TR-89-2133



IMPROVED THERMO-OXIDATIVE-DEPOSITION SCREENING TESTS FOR
TURBINE LUBRICANTS

LARRY FEHRENBACHER
ROBERT SCHAFRIK
JACQUELINE MACIA

TECHNOLOGY ASSESSMENT & TRANSFER, INC.
133 DEFENSE HYW, SUITE 212
ANNAPOLIS, MD 21401

NOVEMBER 1989

FINAL REPORT FOR PERIOD SEPTEMBER 1986 - JUNE 1989

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WRIGHT RESEARCH AND DEVELOPMENT CENTER
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G. A. BEANE IV, Project Engineer
Lubrication Branch
Fuels and Lubrication Division
Aero Propulsion and Power Laboratory



HOWARD F. JONES, Chief
Lubrication Branch
Fuels and Lubrication Division
Aero Propulsion and Power Laboratory

FOR THE COMMANDER



LEO S. HAROOTYAN, JR., Assistant Chief
Fuels and Lubrication Division
Aero Propulsion and Power Laboratory

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REPORT DOCUMENTATION PAGE

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1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS None	
2a. SECURITY CLASSIFICATION AUTHORITY N/A			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for Public Release; Distribution Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A			5. MONITORING ORGANIZATION REPORT NUMBER(S) WRDC-TR-89-2133	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		6a. NAME OF PERFORMING ORGANIZATION Technology Assessment and Transfer, Inc.		
6c. ADDRESS (City, State, and ZIP Code) 133 Defense Highway, Suite 212 Annapolis, MD 21401		6b. OFFICE SYMBOL (If applicable)		
8c. ADDRESS (City, State, and ZIP Code)		7a. NAME OF MONITORING ORGANIZATION Wright Research and Development Center Aero Propulsion & Power Laboratory (WRDC/POSL)		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson Air Force Base Ohio 45433-6563		
8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F33615-86-C-2697		
10. SOURCE OF FUNDING NUMBERS		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
		65502F	3005	20
		WORK UNIT ACCESSION NO. 71		
11. TITLE (Include Security Classification) Improved Thermo-Oxidative Deposition Screening Tests for Turbine Lubricants				
12. PERSONAL AUTHOR(S)				
13a. TYPE OF REPORT Final		13b. TIME COVERED FROM Sep 86 TO Jun 89		14. DATE OF REPORT (Year, Month, Day) October 12, 1989
15. PAGE COUNT 72				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Lubricant, oxidative stability, deposition, thermogravimetric analysis, differential scanning calorimetry, volatility, MIL-L-7808, turbine engine, thermal stability, and screening test		
FIELD	GROUP	11	08	14
				02
19. ABSTRACT (Continue on reverse if necessary and identify by block number) This research applied combined Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) techniques to establish a potential new laboratory screening method for simulating and differentiating the high temperature lubricant degradation phenomena of oils in operational turbine engines.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL G. A. BEANE IV			22b. TELEPHONE (Include Area Code) (513) 255-7463	
			22c. OFFICE SYMBOL WRDC/POSL	

FOREWORD

This final report describes the work performed by Technology Assessment and Transfer, (TA&T) Inc., Annapolis, Maryland, under U.S. Air Force Contract F33615-86-C-2697. The report covers the period from September 1986 to June 1989.

This program, aimed at developing an improved thermal-oxidative testing technique for aircraft turbine engine lubricants, was sponsored by the Wright Research and Development Center, Aero Propulsion and Power Laboratory (WRDC/POSL). The Air Force Project Manager was Mr. Al Beane, IV.

Dr. Larry Fehrenbacher was the principal investigator. He was assisted by Dr. Robert Schafrik and Ms. Jacqueline Macia. The gas-chromatographic-mass spectrometry measurements of lubricant degradation were conducted by Brehm Laboratory at Wright State University, Dayton Ohio. Dr. Tom Tiernan, Director of Brehm Laboratory, assisted in the interpretation and analysis of the results. Special acknowledgements are due the Chemistry Division of the Naval Research Laboratory (Dr. Irwin Singer) for providing TA&T, Inc. with laboratory space in which to conduct the experiments.



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1.0 INTRODUCTION

The continuous introduction of new high temperature materials into advanced, high performance turbine engine design concepts also requires significant improvements in the engine lubricants. These requirements focus on improved thermal-oxidative-degradation properties and, in particular, engine lubricant hot spot deposition characteristics¹. However, for the foreseeable future, bulk oil stability, vapor pressure, and auto ignition temperature properties of engine oils will continue to impose constraints on propulsion system designs.

Collectively, the current turbine oil screening tests are time consuming and provide little insight into the relationship between formulation chemistry [basestock(s) and additives] and fundamental thermal-oxidative-deposition kinetics and mechanisms. The Turbine Oil Oxidation Test (ASTM D-943), for example, requires at least 1000 hours stressing time per test; the Rotating Bomb Oxidation Test (ASTM D-2272) requires 2 to 30 hours per test. These tests are often not sensitive enough to clearly distinguish between the oxidative stability of different formulations². High temperature deposition tests, such as Alcor's High Temperature Deposit, the Vapor Phase Coker, and the Wright Research and Development Center, Aero Propulsion and Power Laboratory's Rotating Cylinder Deposition (thin film) tests are time consuming and can produce very different and occasionally conflicting results. Also, the results correlate poorly with actual turbine operational experience^{3,4}.

The current USAF qualification procedures for MIL-L-7808 turbine oils rely on a suite of laboratory oxidation-corrosion tests, jet engine simulator and full scale jet engine tests to predict in-service performance. These testing procedures are designed to ensure that the candidate oil performs, at the very least, to a level of minimum acceptable quality. For qualification the candidate oil must be within the degradation limits for the measured changes in certain key properties, such as viscosity, total acid number (T.A.N.), alloy coupon weight, and volatile weight loss. However, the results of these laboratory scale and engine simulator tests do not necessarily predict actual engine performance. The complete suite of the qualifying tests can take several months to complete and cost tens of thousands of dollars. The data from these stressing tests only provide limited analytical insight on differences in the physical and chemical properties of the basestocks and the additive packages, particularly, in terms of their influence on the thermal-oxidative-deposition (T.O.D.) behavior of the oil.

Improved turbine engine oil screening tests are needed to accurately assess the capability of present MIL-L-7808-K (proposed new specification) candidate oils to operate at ~205 °C and the new advanced candidate fluids, at 370 °C (i.e. silahydrocarbons, fluorocarbons and phosphazenes). Consequently, a rapid and easy to use test method is required that:

- (1) Simulates the high temperature lubricant degradation phenomena of operational engines;

- (2) Yields quantitative differentiation of the turbine oils' performance based on measurable physical quantities;
- (3) Provides good correlation to in-service results, including remaining useful lubricant life; and
- (4) Produces insight into the basic T.O.D. mechanisms.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques have been widely employed to evaluate thermodynamic physical and chemical properties of automotive and jet engine lubricants^{5,6,7,8}. Previous work has reported excellent DSC data correlation to standard ASTM methods for cloud point (D-2500), pour point (D-97), heat of crystallization and wax content (D-721), melting and crystallization ranges of wax content (D-938, D-127, and D-87), and Rotary Bomb Test (D-2272) for oxidative stability⁹. However, these methods have tended to use test conditions (such as: high pressure oxygen, non-catalytic metal surfaces, and encapsulated pans) which are considerably different from that of a jet engine's operating environment.

This investigation has extended these previous studies by developing DSC and TGA testing procedures and performance parameters which more closely simulate the conditions of an operating jet engine. These procedures offer the following benefits:

- (1) Discrimination between the individual and combined degradation characteristics of evaporation, oxidation, and deposition, enabling these TGA-DSC properties to be combined into a single figure of merit and relative ranking system called VOX-DEP;

- (2) A fast, easy yet sensitive technique requiring only a few milligrams of sample;
- (3) Fundamental insight into the mechanisms and kinetics of the basestock and additive effects on the T.O.D. properties of the fully formulated oils;
- (4) Ability to combine multiple parameters on volatility-oxidation-deposition characteristics in one test run;
- (5) Excellent quality batch control techniques; and
- (6) An improved method for estimating remaining useful lubricant life.

During this investigation, the T.O.D. data, in conjunction with the present MIL-SPEC laboratory bench tests, provided vital information into the oil's extent of degradation and associated volatility, oxidation and deposition characteristics.

The gas chromatography-mass spectroscopy (GC-MS) technique has been shown to be very useful in monitoring additive depletion¹⁰. The GC-MS technique was employed in this investigation to track the changes in the molecular composition of the basestock and the additive concentrations for a MIL-L-7808 Model Oil as thermal-oxidative degradation progressed. This method permitted correlations between the resultant additive concentrations and TGA/DSC results. Based on this insight the GC-MS technique was then applied to oils stressed in the MIL-SPEC oxidation-corrosion and J57 engine simulator tests to further assist in correlating the DSC/TGA results to the current qualification tests. This technique also corroborated the ability of the DSC measurements to predict the remaining useful lubricant life of aged lubricants.

2.0 EXECUTIVE SUMMARY

This research applied combined thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques to establish a potential new laboratory screening method that accurately simulates and differentiates the high temperature lubricant degradation phenomena of oils in operational engines. The following summarizes the results.

- (1) Development of tailored TGA and DSC procedures which combine thermal volatility, oxidation and deposition characteristics of candidate MIL-L-7808 oils into a discriminating figure of merit, called **VOX-DEP**. Key features of VOX-DEP include:
 - (a) A quick, simple, sensitive test of lubricant thermal oxidative stability that uses very small sample sizes; and requires short test times;
 - (b) Performance predictability as confirmed by the data obtained from candidate MIL-L-7808 oils stressed in the MIL-SPEC oxidation-corrosion test and in the J57 engine simulator;
- (2) Quantification of the contributions of basestocks and additives (antioxidant, antiwear, anticorrosion) to the volatility, oxidation and deposition behavior of a Model MIL-L-7808 oil of known composition us-

ing the TGA and DSC methods. Additional DSC/TGA studies provided the following results:

- (a) Defined the pro-oxidant/pro-degradation contributions of bearing wear metals;
- (b) Demonstrated the effects of fresh make-up oil additions on the thermal stability of the used oil.

(3) Application of thermal scanning gas chromatography-mass spectrometry analysis to quantify the relative TGA/DSC thermal oxidative stability results for various MIL-L-7808 oils to differences in chemistry. Specific results included;

- (a) Characterization of the molecular degradation products of the various additives as a function of oxidation temperature and time;
- (b) Correlation of antioxidant concentrations with the DSC oxidative thermal stability of the Model Oil and a series of stressed candidate MIL-L-7808 oxidation-corrosion and J57 engine simulator oils;

(4) FUTURE APPLICATIONS OF THE VOX-DEP APPROACH INCLUDE:

- (a) A method which can be incorporated with the current protocol of MIL-SPEC tests to provide improved discrimination of a candidate lubricant's thermal oxidative stability under stress;

- (b) A technique that can be used to predict the remaining useful life of a lubricant.
- (c) A technique that can readily aid the development of new, high temperature lubricants.

3.0 EQUIPMENT AND OILS STUDIED

3.1 EQUIPMENT

Dupont Model 9900 DSC and TGA, and the Perkin-Elmer DSC-2 and TGS-2, were used to develop the VOX-DEP test procedures that defined the thermal-oxidative-deposition (T.O.D.) characteristics of the oils. The initial screening procedures consisted of placing 0.7 mg of the lubricant sample on a low carbon steel coupon in an aluminum pan under 15 PSI, 55 cc/minute flow of oxygen.

A specially designed pyrolysis probe for a Kratos MS-25 double focusing spectrometer coupled to a Perkin-Elmer Sigma II Gas Chromatograph system (shown in Figure 1) was used to simulate the T.O.D. conditions of the TGA/DSC tests during operation of the mass spectrometer.

3.2 OILS STUDIED

Two different basestocks, four additives and a Model Oil formulation of known composition were used to establish the initial VOX-DEP procedures; three different oil series were then used during the next phase to apply and refine the VOX-DEP procedures. The studied oils are as follows:

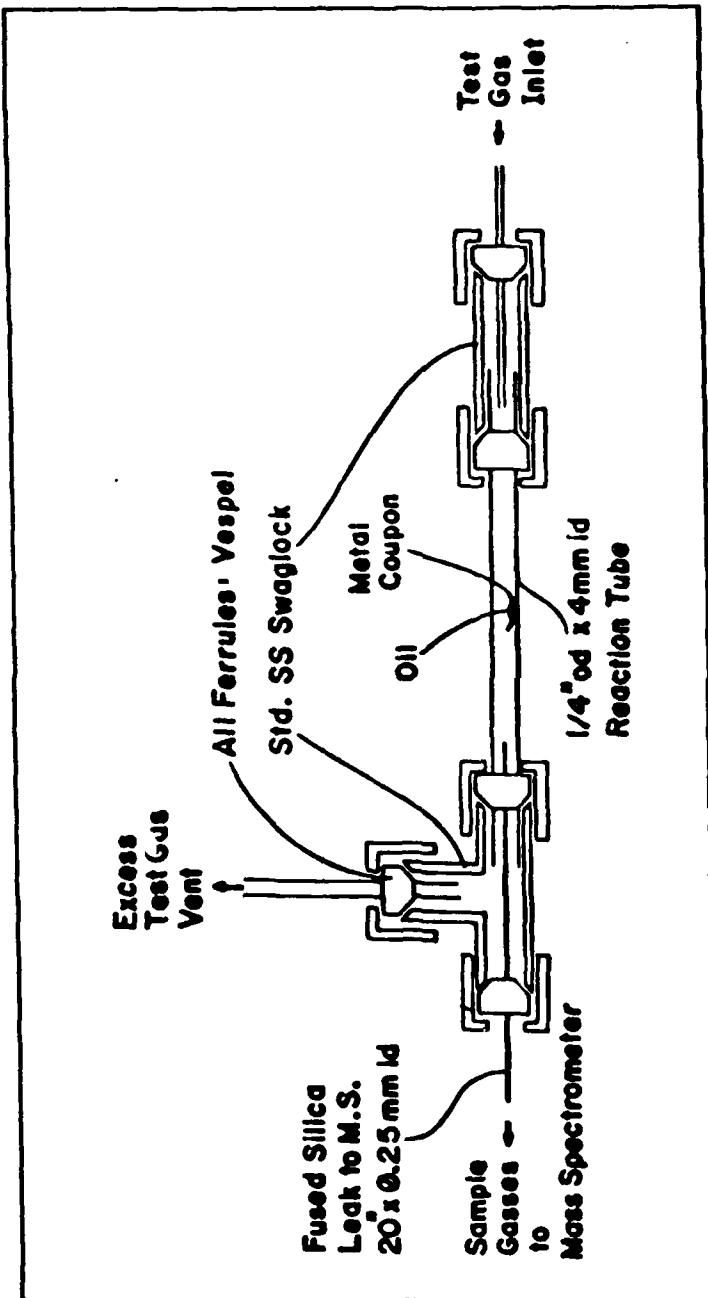


FIGURE 1. CUSTOM LUBRICANT HEATING CHAMBER FOR GC-MS SYSTEM

- (1) Two commonly used MIL-L-7808 basestocks: pentaerythryitol basestock of palmitic acid (*PEPA*), and trimethylolpropane ester of heptanoic acid (*TMPTH*).
- (2) TMPTH basestock plus individual additions of antioxidants: 1 percent dioctyldiphenylamine (*DODPA*) and 1 percent phenyl-alpha-naphthylamine (*PANA*); an antiwear additive: 2.5 percent tricresyl phosphate (*TCP*), a metal passivator additive: 0.02 percent benzotriazole (*BTZ*), and the *Model Oil* which incorporated all of the above mentioned additives.
- (3) A series of fresh candidate MIL-L-7808 oils designated as **TEL 5021-5026**.
- (4) A series of MIL-L-7808 oils that were stressed in the standard Oxidation-Corrosion test (FTMS 5307) designated as **Oils 7021 through 7025**.
- (5) A series of MIL-L-7808 oils which were stressed in the Wright Research and Development Center, Aero Propulsion and Power Laboratory's J57 engine simulator designated as **Oil A (OP-338), Oil B (OP-341) and Oil C (OP-349) series**.

4.0 RESULTS AND DISCUSSION

The VOX-DEP research program was divided into two main phases: Phase I, which consisted of the DEVELOPMENT of the VOX-DEP test procedures; and Phase II, which was the APPLICATION and REFINEMENT of the VOX-DEP procedures. Sections under 4.1 cover the Phase 1 VOX-DEP development and sections under 4.2 and 4.3 cover the Phase 2 VOX-DEP application and refinement work.

In Phase I, the VOX-DEP procedures evolved through a series of TGA and DSC tests on variety of oils using a wide range of experimental test procedures. The final VOX-DEP test procedures were selected by optimizing those parameters that provided the best combination of discrimination, repeatability, sensitivity and operating simplicity.

These initial VOX-DEP procedures were then applied to a series of candidate MIL-L-7808 oils that had been subjected to the MIL-SPEC oxidation-corrosion test and a series of oils that had been tested in the Wright Research and Development Center, Aero Propulsion and Power Laboratory's (WRDC/POS) J57 engine simulator. The VOX-DEP data were compared to the MIL-SPEC oxidation-corrosion test and J57 engine simulator test results in order to assess DSC/TGA capabilities for predicting the performance of both new and aged oils relative to the standard MIL-SPEC viscosity, T.A.N. and deposit rating methods.

The DSC and TGA techniques were also used to determine the pro-oxidative/pro-degradative effects of bearing wear metals on the lubricant's oxidation and volatilization kinetics, and the VOX-DEP

ratings. A gas chromatographic-mass spectrometric technique was used to determine the extent of additive depletion and basestock degradation. It was applied to the Model Oil formulation first and then to oils stressed in the oxidation-corrosion and J57 engine simulator tests.

4.1 VOX-DEP DEVELOPMENT OVERVIEW

The Phase I investigation concentrated on developing test procedures for the following oils: the Model Oil and candidate MIL-L-7808 TEL-5000 series oils.

A Model Oil formulation of known composition and candidate MIL-L-7808 oils were used to establish baseline TGA/DSC test procedures and to monitor the effects of changing test variables on T.O.D. results. The key test variables examined included the following: sample size, scan rate, purge gas, gas pressure, catalytic metals and open/closed sample container. The effect of test parameters on volatility suppression and thermal lag were also investigated. A data base was developed comparing the influence of key test parameters on basestocks, additives and formulations of known composition, prior to performing TGA-DSC tests on a series of candidate MIL-L-7808 oils.

The DSC and TGA instruments were used to study the kinetics of volatility and oxidation of various oils including the contributions of specific additives. The activation energies from a series of isothermal DSC and TGA tests were calculated to obtain insight into the T.O.D. degradation mechanisms.

The GC-MS analysis identified the basestock and additive degradation products and concentrations as a function of temperature. This GC-MS data confirmed that the DSC/TGA tests results accurately reflect basestock degradation and additive depletion rates.

4.1.1 MODEL OIL

TGA testing has been widely used to characterize and assess the thermal induced volatility behavior of petroleum products^{11,12}. Published results have correlated observed volatility characteristics of the lubricant with experimental conditions and lubricant chemistry (such as, the surface area, heating rate, temperature and the percent of non-volatile components).

The initial test procedures involved placing a vented lid (pinhole in the center) on a sample holder containing 0.7 mg of lubricant sample. An oxygen gas purge was regulated at a flow rate of 55 cc/min to prevent anomalous results from residual oil effluents associated with lower flow rates. The oil sample was placed on a C1010 (low carbon steel) coupon to simulate an iron-rich catalytic surface representative of operational engine components. During this study, the onset of volatility was defined as that temperature at which 5 percent weight loss occurred; this offset minimized error in determining the exact point of the thermograph's transition from a horizontal slope to a negative slope. The "fuzziness" of this transition point is possibly due to a slight absorption of water by the sample and variations in the zeroing of the sample holder.

Figure 2 compares the thermograms for the polyol ester MIL-L-7808 basestocks TMPTH and PEPA. As shown, the volatility onset temperatures are very similar (~205 °C). However, beginning at

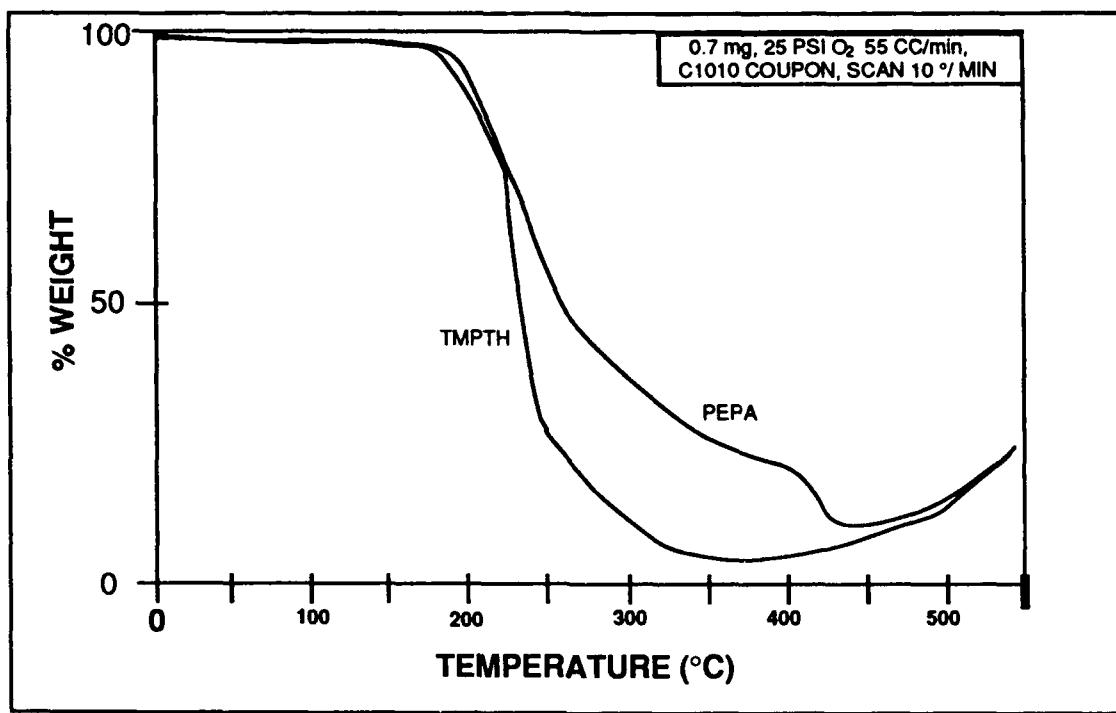


FIGURE 2. COMPARISON OF THE TMPTH AND PEPA BASESTOCK THERMOGRAMS

230 °C PEPA tends to evaporate at approximately a constant rate while the TMPTH follows a logarithmic-type evaporation curve. By 450 °C, the thermograms join and are nearly identical again. These results can be attributed to the differences in the molecular compositions; i.e. differences in the thermal stability of the weakest molecular bonds^{13,14}.

Variations in scan rate, sample size, catalytic surfaces, and pressure had no pronounced effect on the onset of volatility for the TMPTH and PEPA basestocks and the Model MIL-SPEC oil. Also, at the gas flow rate used in this investigation (55 cc/min), no measurable change in the onset of volatility for the basestock TMPTH or the Model Oil was detected for the closed versus the open cup technique.

The relative contributions to the onset of volatility and oxidation, and the percentage of deposits formed, for TMPTH mixed individually with each additive (DODPA, PANA, TCP, and BTZ) and then with the full additive package, (i.e., Model Oil) were investigated. The results are summarized in **Table 1**.

TABLE 1. VOX-DEP DATA FOR A MODEL OIL

SAMPLE DESIGNATION	ONSET OF VOLATILITY*	ONSET OF OXIDATION*	RESIDUE @ 287 °C**
TMPTH	205 °C	215 °C	18 %
0.02 % BTZ + TMPTH	205 °C	208 °C	6 %
2.5 % TCP + TMPTH	208 °C	213 °C	22 %
1 % PANA + TMPTH	203 °C	254 °C	16 %
1 % DODPA + TMPTH	206 °C	247 °C	28 %
MODEL OIL	204 °C	262 °C	34 %

* 0.7mg sample, 25 PSI O₂ @ 55 cc/min, C1010 Steel coupon, 10°/minute
 ** 4 mg sample, 25 PSI O₂ @ 55 cc/min, C1010 Steel coupon, Rapid preheat to 237 °C, scan 2.5°/minute to 287 °C, retained weight residue of original sample

The volatility onset temperature was not influenced by the amount of additives singly or as a group; it remained in the range of 203 °C to 208 °C. Thus, the onset of volatility is primarily a function of the basestock composition itself and not the composition of the commonly used MIL-L-7808 additives. This finding is consistent with the hypothesis that volatilization occurs by the thermally activated breaking of the weak bonds. Therefore, the thermal instability of the weakly bonded basestock components would be much more

significant in influencing the volatilization behavior than the additives which are present in much lower concentrations.

An oxygen environment of 15 PSI and 55 cc/min flow rate was selected for the baseline test parameters to approximate the pressure of an actual engine environment. However, slight deviations from these conditions did not produce appreciable changes in the volatility onset temperatures or weight loss rates.

Oxidation is the major cause of lubricant degradation. During oxidation, the detrimental reactions that occur are reflected by increases in viscosity, total acid number (T.A.N.), metal corrosion, and deposition products, and a decrease in shear stability. However, these measured changes are difficult to correlate quantitatively with the oxidative stability of the lubricant¹⁵. The present MIL-L-7808 bench tests can only monitor these indirect secondary effects, and not the direct chemical changes induced by oxidation. The DSC, which very accurately measures the heat content associated with chemical reactions, is ideally suited for the study of the oxidation stability of petroleum reactions, and their rates^{7,16,17,18}.

At a fixed flow rate of 55 cc/min, increasing the pressure from 15 PSI to 25 PSI for the 0.7 mg PEPA sample produced no noticeable effect on the onset temperature for the primary oxidation peak. Increasing the sample size to 2.0 mg increased the oxidation onset temperature by only 4 °C. This can be attributed to the thermal lag of a larger oil sample. Since this effect was not large, sample sizes of 2 mg or more were occasionally employed to test oils with high volatility. Only slight changes in the primary oxidation peak

temperatures occurred when the scan rate was increased from 10 °C to 20 °C /minute.

The combination of the large sample size (~2 mg) and a slow scanning rate (2.5 °C/minute) yielded the best peak resolution and reproducible results for the PEPA basestock. However, the 0.7 mg sample scanned at a 10 °C/minute rate was selected for the baseline test conditions since it produced rapid yet sufficiently accurate data.

The effect of different metals on the oxidation behavior of the basestocks was as follows:

- (1) The surface dramatically affected the oxidation behavior of the PEPA polyol ester basestock; i.e., the primary oxidation peak shifted from 182 °C for the C1010 steel surface to 210 °C for the aluminum surface;
- (2) The primary oxidation peak broadened by 28 °C on the aluminum surface, reflecting a slower oxidation rate;
- (3) The shape of the primary oxidation peak changed from a strong sharp single peak for iron to a broader double reaction peak for aluminum. This secondary side peak occurs immediately after the primary peak; and
- (4) The secondary exothermic peak for the iron surface occurred at 400 °C. No high temperature peak was observed for the aluminum surface.

As shown, the composition of the metal surface in contact with the lubricant can exert a marked influence on its thermal oxidative

deposition behavior. The iron surface obviously has a strong pro-oxidant effect on the synthetic turbine oil basestock. Accelerated and extensive varnish formation as reflected by the second oxidation peak at 400 °C was also attributed to the catalytic nature of iron. The catalytic effect of an iron surface on the oxidation of petroleum products has been previously reported^{19,20,21,22}. Since normal jet engine usage tends to generate wear particles of iron which are suspended in the oil, an iron coupon (1010 low carbon steel) was selected as the reaction surface for the VOX-DEP test procedures.

The developed DSC test procedures were applied to the basestock (TMPTH), the basestock mixed with individual additives (DODPA, PANA, TCP and BTZ), and the fully formulated Model Oil. Unlike the volatility results, the antioxidant additives had a significant effect on the onset of oxidation, its associated peak width, and the amount of the original sample weight remaining at the onset of oxidation.

BTZ (anti-corrosion agent) and TCP (antiwear agent) had little effect on oxidative stability. Another study has shown that TCP tested on a M-50 bearing steel exhibited a decrease in the coefficient of friction from either the absorption or the decomposition of the TCP additive from the basestock solution at 215 °C²³. This result coincides closely with the observed oxidation onset temperature of 213 °C for TCP. The decrease in the friction that occurred around 215 °C supports the hypothesis of the absorption of the TCP additive components on the surface, as a result of the liberation of the thermal decomposition products of the basestock/additive system.

Oxidation onset temperatures measured for the TMPTH base-stock, the two mixtures containing individual one percent concentrations of DODPA, and PANA, and the Model Oil formulation, were 208 °C, 247 °C, 254 °C and 262 °C, respectively. This trend is consistent with the strength and concentration of the antioxidants, since the Model Oil contains 1 percent of each antioxidant. A previous antioxidant optimal concentration study has noted this phenomenon²⁴.

The DODPA and PANA sample peaks are four degrees wide (considerably narrower than the basestock alone). This peak width was essentially identical to that of the Model Oil formulation. A representative DSC scan, shown in Figure 3, illustrates the differences in oxidation peak widths between the basestock and the Model Oil containing 2 percent of antioxidants. Consequently, the width of the oxidation peak appears to be an indirect measure of the antioxidant's concentration. These DSC curves also revealed the following:

- (1) The antioxidants significantly extend the onset of oxidation temperature; and
- (2) Once the onset of oxidation occurs, oxidation reactions proceed rapidly.

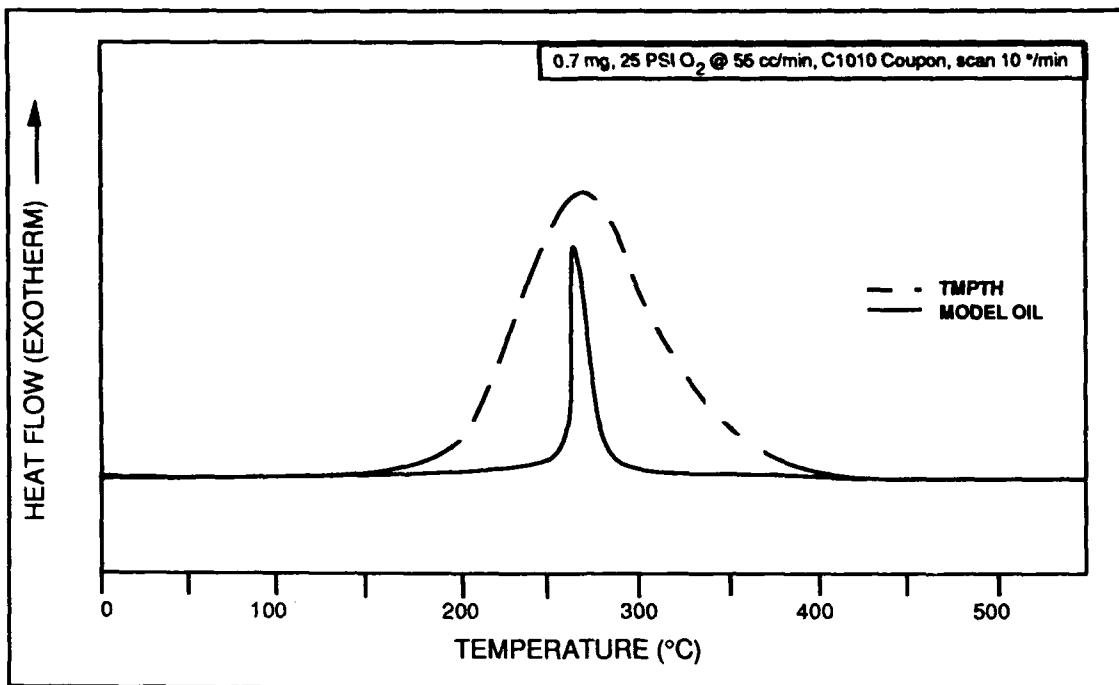
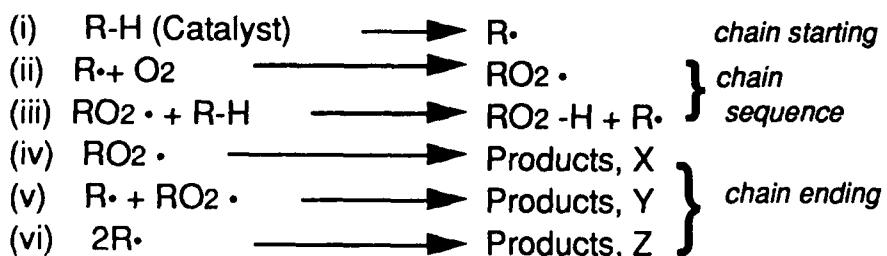


FIGURE 3. DSC SCANS OF TMPTH AND A MODEL OIL

The deposition behavior of turbine oils vary with the chemistry and their associative volatility and oxidation mechanisms^{25,26}. Hydro-carbons follow the general auto-oxidation oxidation scheme shown below:



As indicated above, the termination phase of oxidation results in a viscosity increase of the oil due to the recombination of the hydroperoxide radicals ($RO_2 \cdot$) and the hydrocarbon radicals ($R \cdot$). With

continued oxidation the oxygenated radicals multiply and recombine, eventually growing into high molecular weight decomposition products. Thus, the stability of the polymerized residue is a function of molecular composition such as, number of weak bonds, and length of the thermally decomposed fragments, and the possible locations for the additive/stabilization bonding locations²⁷. The deposits obtained from the scanning TGA tests do not represent equilibrium weights; however, insight into the deposit forming tendencies of the basestocks and formulated oils can be deduced from the obtained data.

In addition, TGA measurements were made at constant temperatures to determine differences in the final equilibrium weights of the various lubricant formulations. Typical isothermal thermograms for the basestock and the Model oil, depicted in Figure 4, illustrate the differences in the rate and amount of residue associated with the additives. As expected, the TGA isotherms reflected no difference in volatility onset temperatures for the basestock and the fully formulated oil. The lower quantity of residue formed by the Model Oil is attributed to presence of antioxidant, metal passivator and antiwear additives. The antioxidants reduce the amount of the hydrocarbon free radical formation, which in turn, reduces the magnitude of the free radical recombination and polymerization reactions.

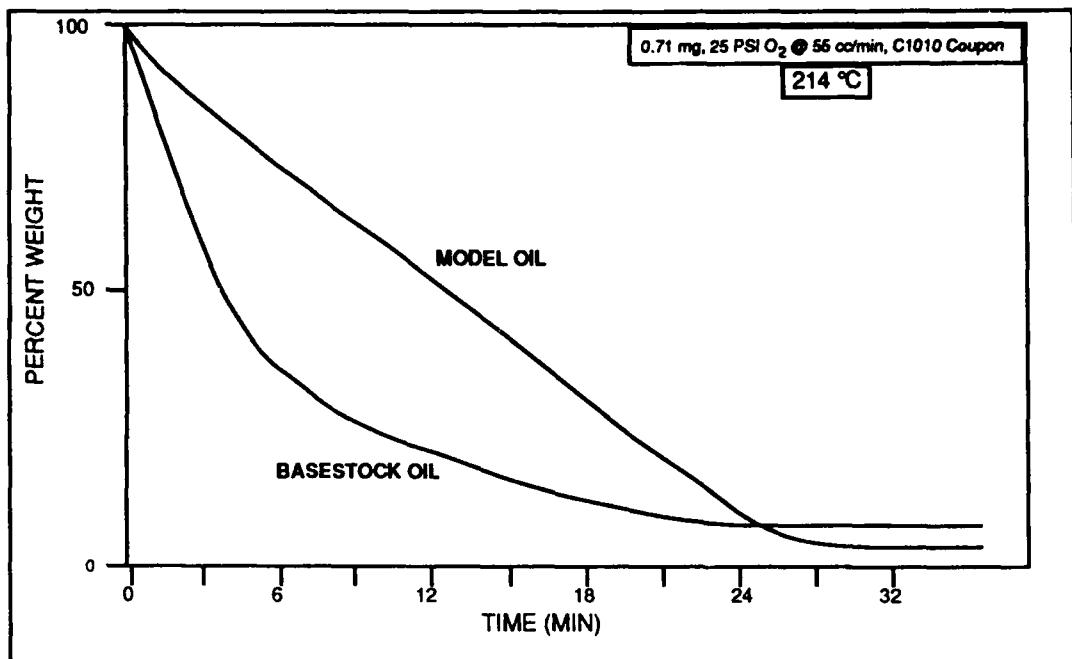


FIGURE 4. THERMOGRAMS OF TMPTH AND THE MODEL OIL

A sharp transition at the final stages of weight loss correlates with the observed sharp transitions seen in the onset of the oxidation for the scanning and isothermal DSC results for the Model Oil formulation. This transition is attributed to the rapid increase in the degradation/polymerization process due to the depletion of the antioxidants.

The time to form the equilibrium amount of oxygenated polymerized residue for TMPTH decreased as the isothermal temperature increased as expected for a thermally activated process. That residue formation decreased as the isothermal temperature increased, most likely, is attributed to the decrease in the amount of free radicals present, polymerization time and/or stability of the residue. A previous deposition study has noted that the main polymerization process occurs between 260 °C and 280 °C. Furthermore,

isothermal temperature of 280 °C is representative of hot spot temperatures found in jet engines²⁶.

4.1.2 CANDIDATE MIL-L-7808-5000 SERIES OILS

The developed TGA/DSC test procedures described in the previous section were applied to a series of fresh MIL-L-7808 candidate turbine oils. These oils (TEL 5021-5026) are proprietary formulations which, in some cases, are similar, to the composition of the Model MIL-SPEC Oil. Almost all suppliers use similar additive packages which suggests that only slight variations in the chemistry and concentrations of specific additives are likely.

Volatility, Oxidation and Deposition Characteristics

The volatility, oxidation, and deposition (VOX-DEP) data on the 5000 series oils are summarized in tabular form in **Table 2** and described in the subsequent text. Increasing the sample size from 0.7 mg to 2.0 mg and slowing the scan rate from 10°C to 5 °C/minute did not produce a significant difference in the volatility onset temperature for any of the oils in this series. The volatility characteristics of the 5000 series can be divided into two groups: Group 1 consisting of oils 5021, 5022, and 5025 with volatility onset temperatures around 180 °C; and Group 2, consisting of oils 5023, 5024 and 5026, with volatility temperatures around 195 °C. These data suggest that Group 2 contains a higher percentage of thermally stable basestocks.

TABLE 2. DSC AND TGA RESULTS FOR CANDIDATE OILS 5021 THROUGH 5026

SAMPLE DESIGNATION	ONSET OF VOLATILITY*	ONSET OF OXIDATION**	PERCENT RESIDUE***
5021	184 °C	253 °C	2 %
5022	179 °C	255 °C	13 %
5023	197 °C	260 °C	2 %
5024	197 °C	247 °C	3.5 %
5025	182 °C	243 °C	5 %
5026	192 °C	183 °C	6 %

* 0.7 mg sample, 25 PSI, O₂ @ 55cc/min, C1010 Steel coupon, 10°/min
 ** 4 mg sample, 25 PSI, O₂ @ 55cc/min, C1010 Steel coupon
 *** 0.7 mg sample, 25 PSI, O₂ @ 55cc/min, C1010 Steel coupon, rapid preheat to 267 °C, hold isothermally

With the exception of oil 5026, the oxidative stability of this oil series is similar. Since the previous Model Oil and individual additive studies had shown that the width of the oxidation peaks are directly related to the antioxidant concentration levels, the broad peak width of oil 5026 suggests that it has far less antioxidant than the other oils. Oxidation peak widths alone, however, should be used cautiously for the relative ranking of oils because there are variations in the stabilities and chemistries of the basestock mixtures used by different formulators.

The deposit results for the 5021-5026 candidate oils are also presented in Table 2. The deposit forming tendencies of the candidate oils were examined using a scanning DSC run that included an isothermal hold for 15 minutes at 267 °C. The isotherm at 267 °C was above the oxidation onset temperature of the oils. Oils 5021 and 5023 formed the least amount of deposit with values of 2 percent, followed by oils 5024, 5025, and 5026 with 3.5 percent, 5 percent

and 6 percent, respectively. Oil 5022 produced a much larger deposit, yielding a residue that was 13 percent of the original lubricant sample weight.

The very heavy deposit forming tendency of Oil 5022 versus the other oils was corroborated by sequential scanning DSC-scanning TGA measurements in which the residues from 4 mg DSC samples were removed after completion of the primary oxidation process and then scanned in the TGA. Even though the residues from the scanning DSC tests did not represent equilibrium weights, the subsequent scanning weight loss measurements in **Figure 5** clearly show that the Oil 5022 residue from the DSC test retained the largest percentage of its original weight even up to temperatures in excess of 500 °C.

The slight differences in oxidation onset temperatures prompted a series of induction time measurements at 227 °C as a function of oxygen pressure to determine if a specific set of isothermal conditions could improve the discrimination capabilities of the DSC method. As reflected by the data in **Table 3**, ranking the oxidation stabilities of the 5021-5026 series by isothermal DSC techniques revealed two problems:

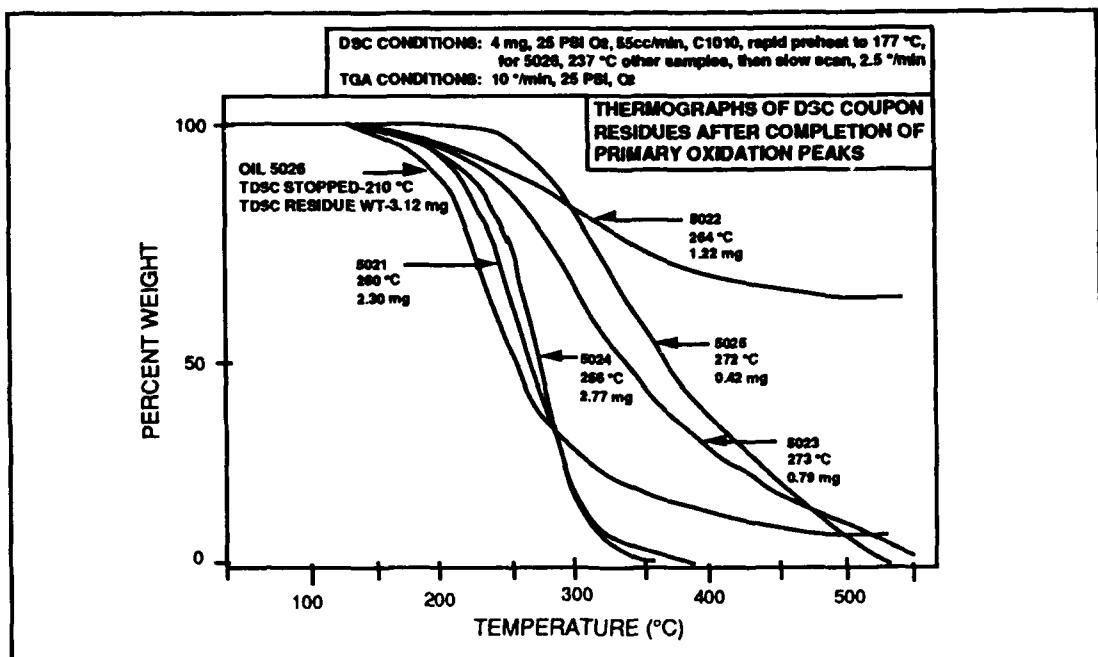


FIGURE 5. THERMOGRAMS OF OILS 5021-5026 RESIDUES

- (1) The low oxidative stability of oil 5026 made it impossible to find an isotherm at which all the oils exhibited reasonable induction times; as reflected by the broad peak width, oil 5026 probably contains a marginal antioxidant concentration and probably would not qualify as a MIL-SPEC lubricant:
- (2) Testing at higher oxygen pressures, while compressing the oxidation onset times, adversely affected discrimination; i.e. the oxidation onset times approached each other rather than separated the distinction between the various oils at this selected isothermal temperature. (Note: The reason that oxidation onset times for some oils decreased and then began to increase as the oxygen pressure

increased is not known. However, it may be due to a change in kinetics as a result of reactions occurring with additives in addition to the anti-oxidants.)

TABLE 3. ISOTHERMAL DSC OXIDATION RESULTS AS A FUNCTION OF O₂ PRESSURE FOR CANDIDATE OILS 5021-5026

Sample Designation	ISOTHERMAL DSC OXIDATION INDUCTION TIMES (MIN) 227 °C			
	25	50	95	150
5021	47	23	25	28
5022	NR	27	25	29
5023	41	19	20	28
5024	NR	24	10	17
5025	NR	60	27	35
5026	0	0	0	0

0.7 mg. @55 cc/min, C1010, Preheated to 227 °C in Nitrogen

NR -No Results due to Inordinately Long Induction Times

However, relative ranking of the oils are generally maintained with the isothermal tests. Therefore, it was concluded that low oxygen pressure (15 psi was eventually selected) is desired, since it is closer to the pressures of the the engine environment yet provides excellent discrimination between the candidate oils.

4.1.3 VOX-DEP RATING SYSTEM

An overall ranking system, called the VOX-DEP, was developed to combine an oil's individual characteristics of volatility, oxidation and deposition into a single figure of merit. The methodology of the VOX-DEP approach is as follows: for each characteristic, the oil with the superior property is assigned a relative ranking (RR) of one; the next best is assigned two, etc. In case of a tie, the same RR is given to both oils. For the 5021-5026 series, equivalent rankings were assigned to oils whose volatility onset temperatures were within 3 °C of each other; similarly, oils with oxidation onset temperatures within 3 °C and deposit varnish weight differences within 3 percent were assigned the same RR. Then, the RR rating for volatility, oxidative stability, and deposition were linearly combined (i.e. added together) to provide an overall ranking, or figure of merit. The oil with the lowest score is ranked the best (least degradation) and the oil with the highest score is ranked last (greatest degradation).

This algorithm is summarized in **Table 4** below:

TABLE 4. VOX-DEP METHODOLOGY - PHASE I

RELATIVE RANKING ALGORITHM

BEST CATEGORY IS ASSIGNED VALUE 1, NEXT BEST IS 2, ETC

- VOLATILITY ONSET TEMPERATURE:
 - ESTABLISH CATEGORIES SEPARATED BY 3 °C (HIGHEST ONSET IS 1)
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
- OXIDATION ONSET TEMPERATURE:
 - ESTABLISH CATEGORIES SEPARATED BY 3 °C (HIGHEST ONSET IS 1)
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
 - OILS WITH AN OXIDATION ONSET TEMPERATURE ≤ 220 °C ARE RANKED * (UNACCEPTABLE)
- DEPOSITION DATA:
 - ESTABLISH CATEGORIES SEPARATED BY 3 PERCENT RESIDUE (LOWEST RESIDUE IS 1)
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
- LINEARLY ADD THE RANKINGS
- THE OIL WITH THE LOWEST SCORE IS RANKED FIRST, ETC

This initial VOX-DEP rating system was based on combined TGA and DSC test results. Rapid scan TGA results were used to determine the volatility tendency; oxidation and deposition results were based on 4.5 mg samples that were rapidly preheated to 220 °C, then slow scanned at 5 °/min to 287 °C and finally held at 287 °C for 30 minutes. This VOX-DEP rating algorithm was applied to the candidate MIL-L-7808 5021-5026 series data in **Table 2**, and is summarized

in Table 5. Note that the application of the algorithm results in Oils 5025 and 5026 having different Deposition ratings even though their Percent Residue (from Table 2) only differed by 1 percent; this is due to the fact that the start of the category for the 1 rating was established by Oils 5021 and 5023 at 2 percent residue, and adding the category width of 3 percent resulted in any oil with a Percent Residue between 2 and 5 being assigned a rating of 1.

Since no data on the performance of these oils in engine simulator or full scale engine tests were available, it was not possible to judge the predictive capabilities of the VOX-DEP ratings for these oils. The VOX-DEP system was later compared to MIL-SPEC oxidation corrosion tested oils and to actual J57 engine simulator results and refined accordingly. These results are described in Sections 4.2 and 4.3, respectively.

TABLE 5. VOX-DEP RANKING OF CANDIDATE OILS 5021 THROUGH 5026

MIL-L-7808 SAMPLE DESIGNATION	VOLATILITY TENDENCY	OXIDATION TENDENCY	DEPOSITION TENDENCY	OVERALL RANKING
5021	3	2	1	3
5022	3	2	3	4
5023	1	1	1	1
5024	1	3	1	2
5025	3	4	1	4
5026	2	-	2	-

NOTE: RATING 1 IS BEST, 2 IS NEXT BEST, ETC.
* FAILED MINIMUM VALUE.

4.1.4 KINETIC AND DEGRADATION MECHANISMS

Volatility And Oxidation Kinetics Results

Isothermal TGA tests were performed to obtain insight into the kinetics of volatilization. The Model Oil formulation and candidate MIL-L-7808 Oil 5025 were compared. Arrhenius plots showed no slope changes within the temperature region studied. Model Oil and candidate Oil 5025 activation energies for volatilization, depicted in **Figure 6** are based on times to reach a 50 percent weight loss in isothermal TGA tests. The calculated activation energies for the volatilization of these oils was 23 kCal/mole, suggesting very similar basestock chemistries.

The Model Oil and the candidate MIL-SPEC 5025 oil were subjected to a series of isothermal DSC tests to investigate the kinetics of oxidation. The activation energies for oxidation onset times were calculated from the Arrhenius plots shown in **Figure 7**. The calculated oxidation activation energy value is 34 kCal/mole for both the tested oils. This value is approximately 50 percent greater than the energy needed for volatility (23 kCal/mole). The volatilization activation energy is lower since it represents the loss of the lighter weight and thermally unstable molecular components of the basestock. These results are consistent with activation energies expected for the evaporation and oxidation of hydrocarbon based lubricants.

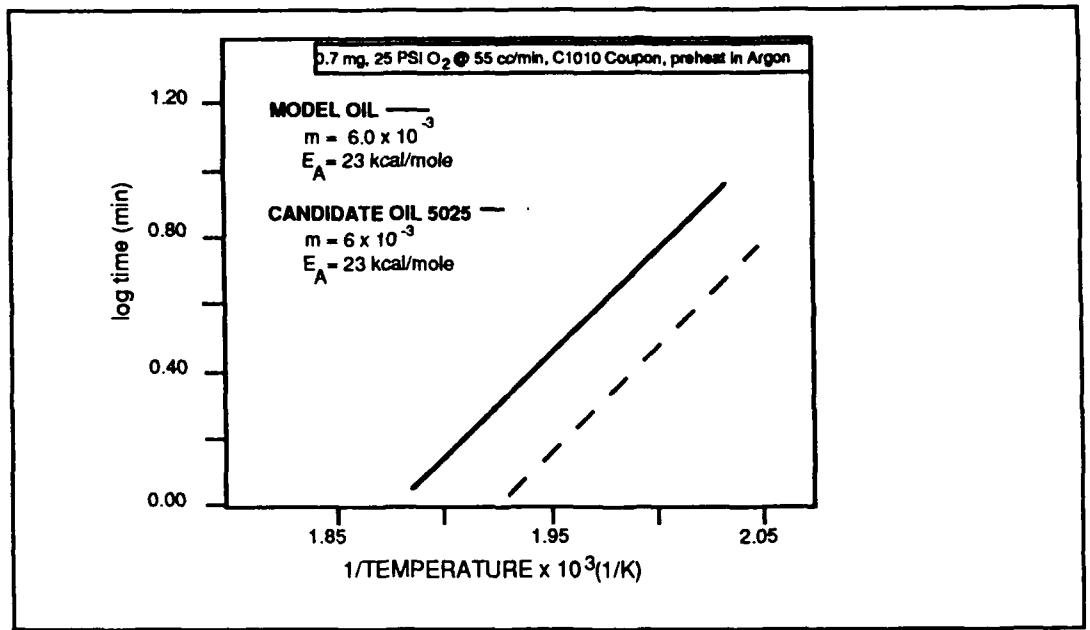


FIGURE 6. ACTIVATION ENERGY OF VOLATILITY FOR A MODEL OIL AND CANDIDATE OIL 5025

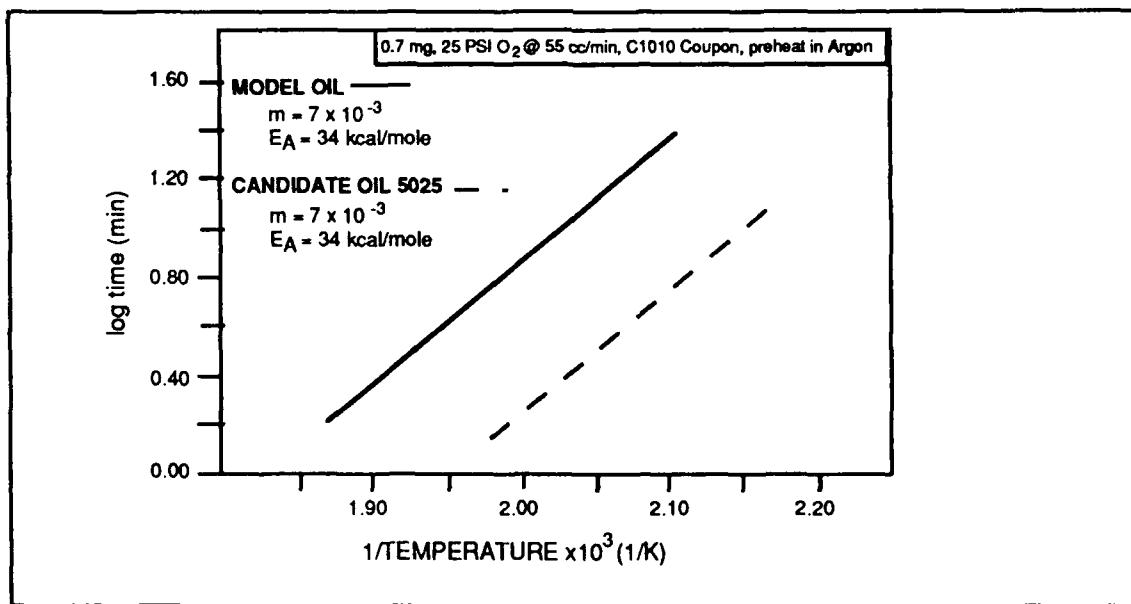


FIGURE 7. ACTIVATION ENERGY OF OXIDATION FOR A MODEL OIL AND CANDIDATE OIL 5025

Thermal Scanning Gas Chromatographic-Mass Spectroscopy Analysis

Aliquots of lubricant formulations were placed on 1010 steel coupons and each coupon was inserted in the custom designed pyrolysis chamber was shown diagrammatically in **Figure 1**. The chamber was installed in the oven of the gas chromatograph which is an integral part of the GC-MS system described above. At the start of each GC-MS run, the flow of gas was established (2.8 cc/min), and the temperature of the oven was raised to 60 °C and held for 5 minutes. The temperature was then increased at a rate of 10 °C/min. Once the column oven attained 140 °C, mass spectral scanning was begun and continued for 30 minutes. When the pyrolysis chamber reached 300 °C, the temperature was held constant for approximately ten more minutes until mass spectral scanning was completed. The mass spectrometer scanned repetitively over the mass range of $m/z = 27$ to $m/z = 500$ during the heating cycle and the resultant spectra were continuously recorded.

The summary of the results for the thermal scanning mass chromatographs of TMPTH, TMPTH + 1 percent DODPA, and the fully formulated Model Oil (1 percent DODPA and 1 percent PANA) is presented in **Figure 8**. These data were obtained under test conditions similar to the scanning TGA experimental runs. The findings displayed a strong correlation with the TGA onset of volatility temperatures and DSC oxidation peak widths on the same samples (see **Table 1**). The geometry of peak shapes from the mass

scans is very similar to the scanning DSC peak shapes, previously illustrated in **Figure 3** for the TMPTH and Model Oil.

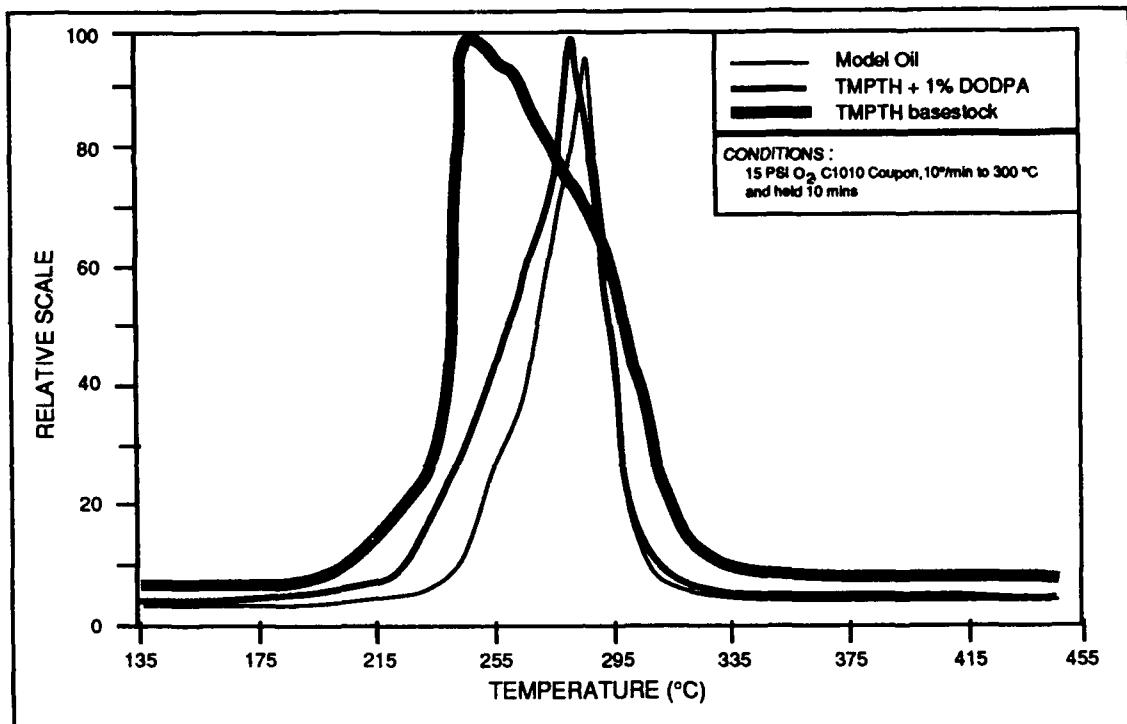


FIGURE 8. THERMAL SCANNING MASS CHROMATOGRAMS OF A MODEL OIL SERIES

The evolution of volatile compounds was nearly complete by 300 °C for the basestock and the additive formulations. One percent addition of DODPA to the TMPTH basestock substantially reduced the rate of oxidation. The peak ion intensity for TMPTH occurred at 245 °C, while the two samples containing antioxidants peaked at 270 °C. The mass spectrometer identified four unique ion masses at $m/z = 43$, $m/z = 85$, $m/z = 113$, and $m/z = 341$ for the thermal decomposition of the TMPTH basestock. These evolved species are a result of the oxidation decomposition reaction of the thermally weak

bonds of the TMPTH molecule. The evolved species are the propyl ion, the heptyl ion, the heptanoyl ion, and the TMPTH molecule minus the heptanoyl acid moiety. **Figure 9** depicts how TMPTH basestock decomposes into various fragment species. These results are in agreement with previous work with TMPTH²⁸. The distribution of major ionized fragments during the thermal scan aided in the understanding of chemical degradation mechanisms. The relative fragment distribution is summarized in **Table 6**. These data clearly indicate that the fully formulated Model Oil retains substantially more of the parent molecule identity ($m/z=341$) than either the TMPTH + 1 percent DODPA or the TMPTH basestock itself. The temperatures of 279 °C and 255 °C at which the greatest intensity of the parent molecule is seen for the Model Oil and TMPTH +1 percent DODPA agrees in general with the oxidation peak maximum temperatures of 270 °C and 245 °C, respectively from the DSC scans.

The large percentage of the parent molecule detected near the volatility peak reveals the protective nature of the antioxidant in suppressing basestock volatility. A substantial increase in the temperature at which the parent molecule evolves is obtained from the addition of 1 percent DODPA. Thermal scanning mass chromatograms were analyzed for the presence of unique ions associated with the individual additives. Two unique ions at mass to charge ratios of 64 and 91 for BTZ; 107 and 368 for TCP; 251 and 322 for DODPA; 108 and 115 for PANA, were identified. Close inspection of these data displayed in **Table 7** revealed some interesting insights into the behavior of the individual additives.

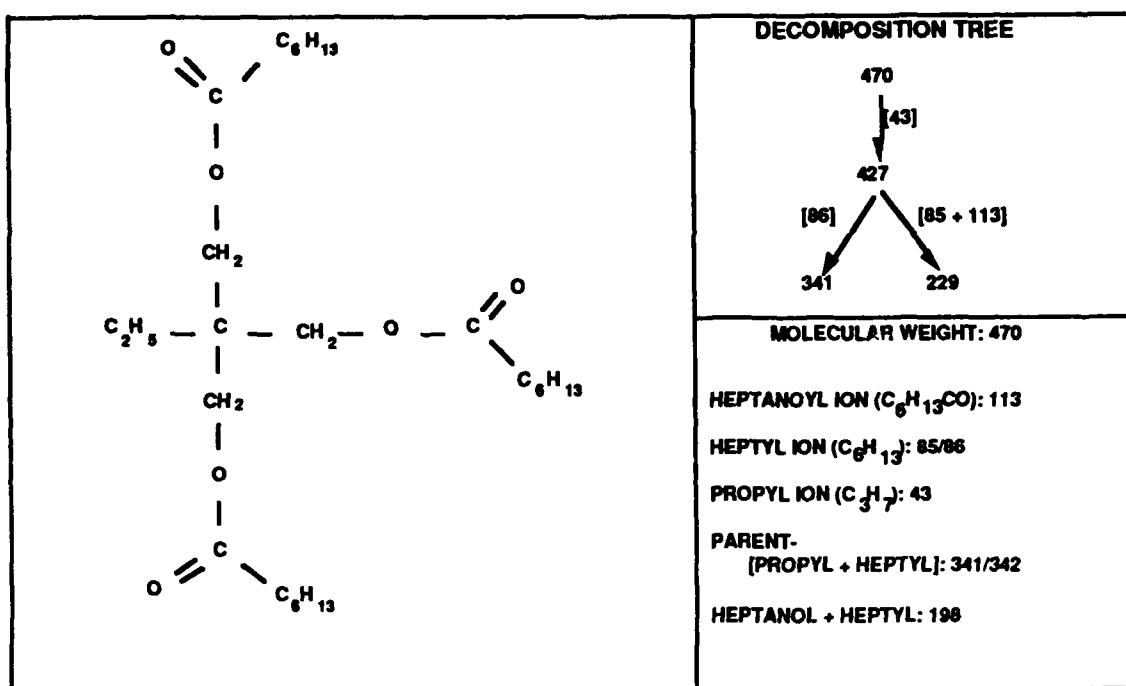


FIGURE 9. MOLECULAR DECOMPOSITION TREE FOR TMPTH (TRIMETHYLOLPROPANE TRIHEPTANOATE)

The unique additive peaks are readily identifiable even at low concentrations. Thus, ability to quantify concentrations of additives in used oil appears to be feasible. Possible chemical degradation mechanisms can be inferred from the unique ion peaks of the additives, and correlated with other detrimental effects such as wear, corrosion and hot spot deposition experienced by operational engines. Subsequent GC-MS analysis and stressed oils presented in the next section enabled additive depletion rates to be correlated quantitatively with DSC results

TABLE 6. RELATIVE DISTRIBUTION OF TMPTH IONS USING MASS SPECTROMETRY

TEMP	PROPYL ION M/Z 43	HEPTYL ION M/Z 85	HEPTANOYL M/Z 113	TMPTH MINUS M/Z 341
TMPTH BASESTOCK				
235 °C	100 %	42 %	77 %	3 %
243 °C	100 %	46 %	78 %	4 %
251 °C	100 %	47 %	83 %	6 %
275 °C	100 %	37 %	88 %	5 %
295 °C	76 %	18 %	64 %	0 %
TMPTH +1 % DODPA				
235 °C	97 %	23 %	74 %	0 %
255 °C	100 %	60 %	94 %	13 %
279 °C	100 %	34 %	86 %	4 %
MODEL OIL				
235 °C	100 %	42 %	93 %	7 %
255 °C	100 %	71 %	92 %	23 %
279 °C	100 %	68 %	83 %	22 %
287 °C	100 %	42 %	87 %	7 %

TABLE 7. UNIQUE ADDITIVE IONS USING MASS SPECTROMETRY

MASS TO CHARGE RATIO			
BTZ	TCP	DODPA	PANA
252	368	322	252
250	367	251	217
235	233	250	115
233	219	235	
219	165	97	
	122		
	121		
	108		
	107		
	106		
	105		
	104		
	103		
	93		
	92		
	90		

NOTE:
TABLE LISTS IONS GREATER
THAN 90 AMU WITH AN
INTENSITY GREATER THAN 1 %

4.2 VOX-DEP APPLICATION AND REFINEMENT

The Phase II program was divided into two main parts: the application (and modification) of the developed VOX-DEP test procedures to oxidation-corrosion tested oils (described in Section 4.2.1) and to J57 engine simulator tested oils (described in Section 4.3.1). The correlations between the VOX-DEP rankings with the physical-chemical changes (e.g. viscosity and total acid number) are presented, and oils are ranked relative to each other. The statistical effect of several experimental variables was also investigated. For example, the statistical sensitivity of scan rate on the onset of oxidation temperature and the percent residue was determined. DSC isothermal tests and gas chromatography-mass spectrometry were used to gain further insight into the degradation kinetics and mechanisms of the stressed oils.

A key objective of the analysis of the oxidation-corrosion tested candidate MIL-L-7808 oils was to correlate current MIL-SPEC performance test results with VOX-DEP ranking analysis, thereby enhancing the capability of the VOX-DEP approach to screen-out marginal lubricants prior to stressing in expensive, time consuming qualification tests. For instance, operational costs of the full-scale J57 engine test can exceed \$100,000 for a 100 hour test; the analysis costs of the aged oil samples are additional costs.²⁹ An additional objective was the prediction of the remaining useful life of stressed lubricants using the VOX-DEP procedures.

4.2.1 VOX-DEP RESULTS WITH OXIDATION-CORROSION TESTED OILS

A series of five candidate MIL-L-7808 oils designated TEL-7021 through 7025 which had been subjected to 96 hours in the standard MIL-L-7808 oxidation-corrosion test (200 °C) in the presence of iron, silver, bronze, aluminum, magnesium, and titanium metals were evaluated with the VOX-DEP procedures. Aliquots of oils 7021 through 7025 that were withdrawn at successive 8 hour intervals during the 96 hour test were provided by the Wright Research and Development Center, Aero Propulsion and Power Laboratory (Mr Al Beane IV).

Volatility Results

The scanning and isothermal TGA/DSC test results on the fresh (0 hours) and 96 hour oxidation-corrosion tested 7021 through 7025 oils are summarized in **Table 8**.

For the fresh oils, the onset of volatility can be divided into 3 groups. Group 1 contains oils 7021 and 7022, which displayed low onset of volatility temperatures of 196 °C and 208 °C, respectively. Group 2 Oils 7023 and 7025 exhibited midrange values of 215 and 216 °C, respectively, while Oil 7024 was by itself at 226 °C. For the oils stressed 96 hours in the oxidation-corrosion test, the onset of volatility measurements were made on Oil 7022 and Oil 7025, only.

TABLE 8. DSC AND TGA RESULTS FOR CANDIDATE OILS 7021 THROUGH 7025

SAMPLE DESIGNATION	TIME STRESSED IN OXIDATION-CORROSION TEST	ONSET OF VOLATILITY*	ONSET OF OXIDATION*	RESIDUE
7021	0 hours 96 hours	196 °C not tested	256 °C 227 °C	1 %
7022	0 hours 96 hours	208 °C 213 °C	257 °C 233 °C	1.5 %
7023	0 hours 96 hours	215 °C not tested	255 °C 219 °C	1 %
7024	0 hours 96 hours	226 °C not tested	252 °C 233 °C	2 %
7025	0 hours 96 hours	216 °C 163 °C	198 °C 240 °C	5 %

* 0.7 mg sample, 25 PSI O₂ @ 55 cc/min, C1010 Steel coupon, 10°/min

The thermograms for the fresh and 96 hour aged 7022 oil samples shown in **Figure 10a** were similar indicating minimal degradation in oil properties. The increase of 5 °C in the onset of volatility for the aged 7022 can be attributed to both the loss of a small quantity of low molecular weight (LMW) components and an increase in higher molecular weight oxidized fragments during the 96 hour oxidation-corrosion test. The temperature at which 50 percent weight loss occurs increased by only 13 °C between the fresh and 96 hour samples suggesting that excessive polymerization did not occur during the 96 hour oxidation-corrosion test. These findings are in agreement with other reported work on the degradation of synthetic oil formulations.³⁰

The thermograms for the fresh and 96 hour oxidation-corrosion stressed Oil 7025 are shown in **Figure 10b**. The volatility onset temperature of the 96 hour sample decreased 53 °C and the 50 percent weight loss temperature increased 80 °C. The loss of

volatile products (LMW) at lower onset temperatures, and the large increase in the 50 percent weight loss temperature is indicative of extensive radical formation and oxygenated polymerization of the remaining molecular fragments. The TGA curves for oil 7022 and 7025 clearly demonstrates that the oxidative stability of the aged oil sample 7022 is preserved in comparison to the extensive degradation experienced by oil 7025. These curves also highlight the significance of using the volatility onset and the 50 percent weight loss temperatures to characterize the extent of lubricant degradation by the thermogravimetric analysis method.

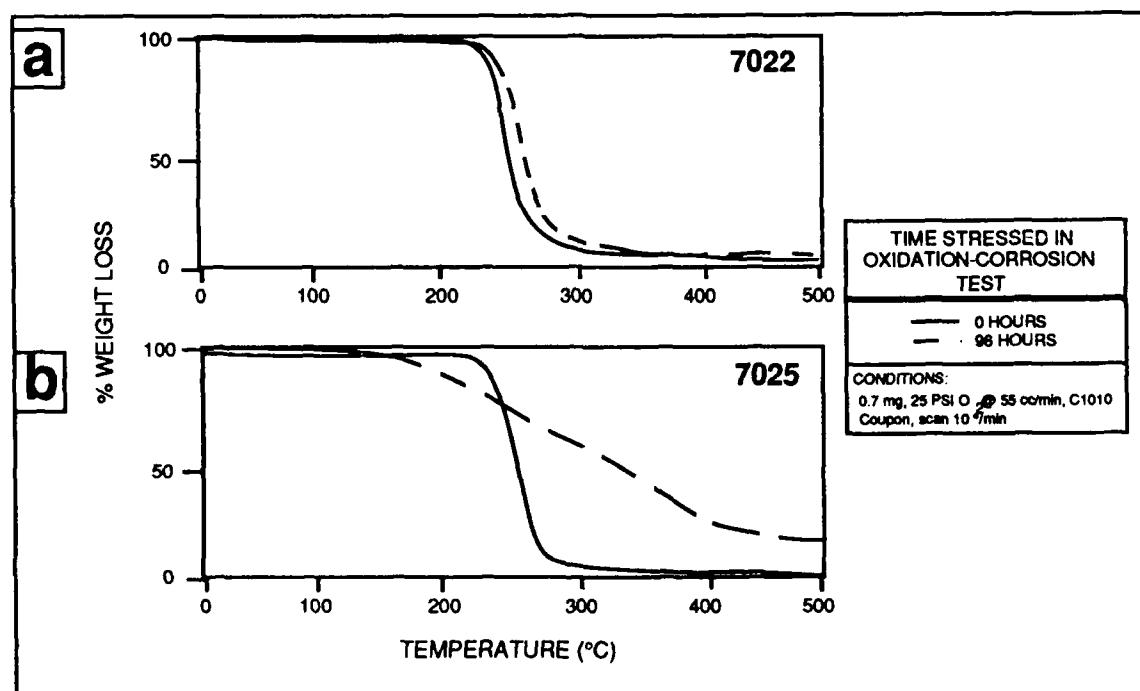


FIGURE 10. THERMOGRAMS OF CANDIDATE OILS 7022 AND 7025

Oxidation Results

The oxidation onset temperature for all the fresh oils were similar except for oil 7025, whose 200°C onset temperature is approximately 50°C lower than the other oils. This result, even in the absence of any other data, suggests that oil 7025 would be incapable of passing the standard MIL-L-7808 oxidation-corrosion test.

The oxidation onset temperatures for the fresh and aged oils plotted as a function of time in the oxidation-corrosion test, are shown in **Figure 11**. The key findings from these scanning DSC tests as well as isothermal tests are as follows:

- (1) All oils, except for oil 7025 experienced an approximately linear decrease in the oxidation onset temperature with time indicative of a gradual reduction in their oxidative stability and corresponding antioxidant concentrations.
- (2) Oil 7025 experienced an initial decrease in the oxidation onset temperature after 16 hours of testing, followed by an continual increase with subsequent test time. The initial decline can be attributed to the initial oxidative degradation of the basestock. The apparent increase in oxidative stability is actually a measure of the degree of excessive polymerization that occurs with increased test time.
- (3) The similarity of the oxidation onset temperatures between 24 through 48 hours for all the oils, except for oil 7025, reflects the relatively good oxidative

stability of these candidate MIL-L-7808 oil formulations.

- (4) The divergence in the oxidative stability of the aged samples after the 48 hours suggests that certain oils have reached additive depletion levels where the rate of oxidative polymerization is increasing.
- (5) Isothermal DSC tests provide better oxidative stability discrimination than the DSC scanning technique. For example the isothermal results, summarized in **Table 8**, provided discrimination between oils 7021, 7022 and 7023 although they exhibited nearly identical oxidation onset temperatures in the scanning mode.

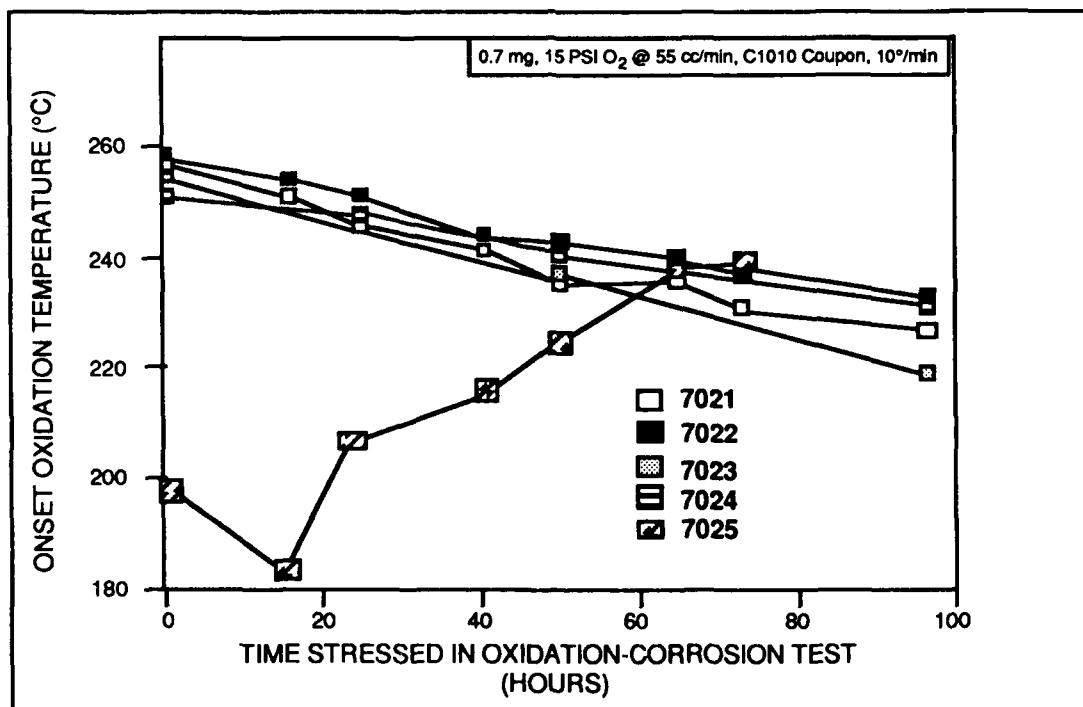


FIGURE 11. OXIDATION ONSET FOR CANDIDATE OILS 7021 THROUGH 7025

Oxidation peaks widened appreciably as the oils were stressed in the oxidation-corrosion test, as depicted in Figure 12 a and b for oils 7022 and 7025. Fresh 7025 underwent thermal-oxidative degradation almost immediately upon start of the test. The other oil formulations were better protected from oxidation, thus preventing the early detrimental effects experienced by oil 7025. The combination of low onset temperature and broad width of the oxidation peak of oil 7025 suggests that the antioxidant concentration is very low, if not totally absent.

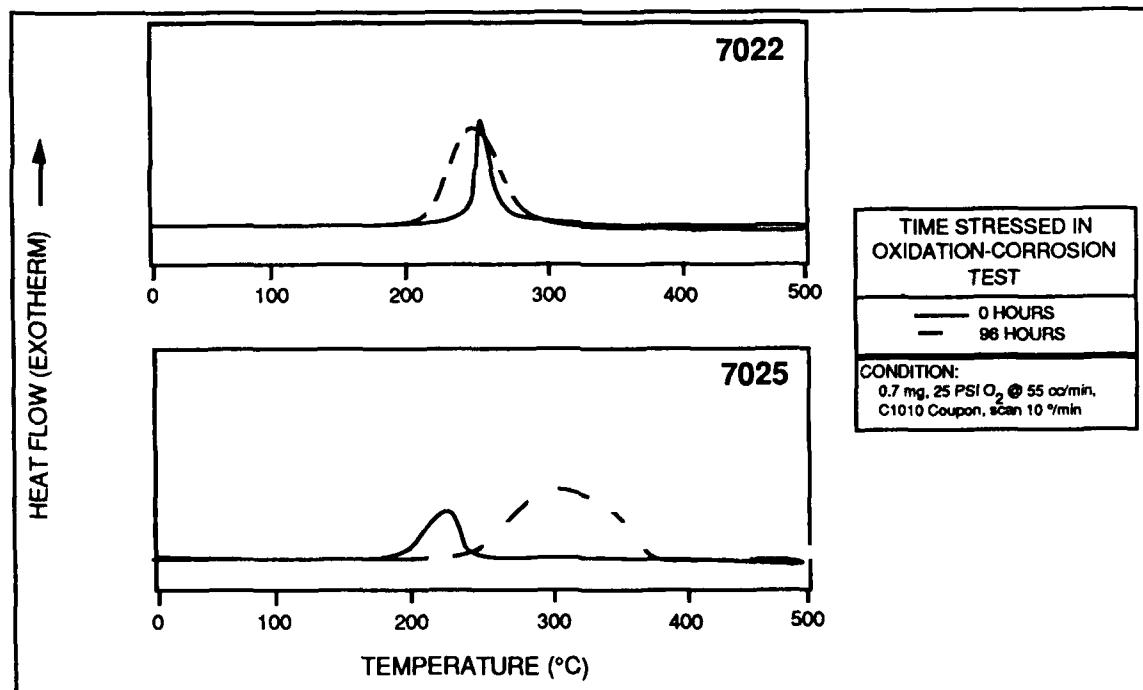


FIGURE 12. DSC SCANS FOR CANDIDATE OILS 7022 AND 7025

It was subsequently determined that Oil sample 7025 was just a basestock (i.e., no additives) which accounted for the extremely

poor VOX-DEP behavior. The series of DSC oxidation curves for the Oil 7025 oxidation-corrosion test series in Figure 13 graphically depicts the rapid extensive degradation that occurs once antioxidants are depleted.

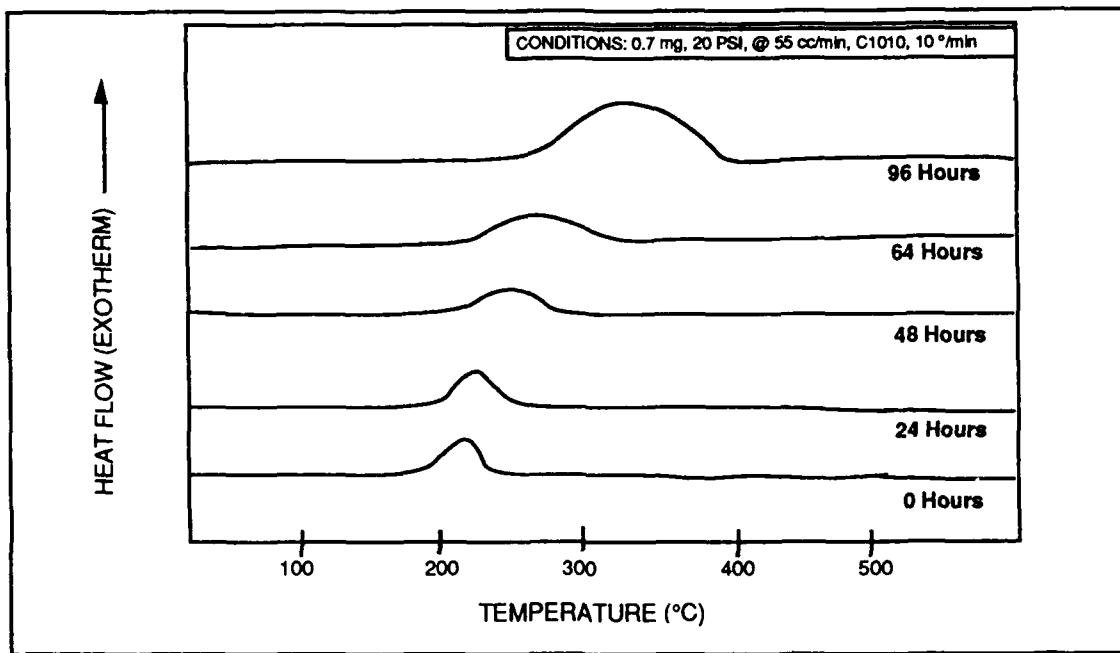


FIGURE 13. DSC SCANS OF OXIDATION-CORROSION TESTED OIL 7025 SHOWING EXCESSIVE DEGRADATION

One last set of tests that were performed involved experimental statistical repeatability. A scan through the oxidation peak followed by a isothermal hold was used to measure oxidation and deposition characteristics. Sample sizes of approximately 1.3 mg oil were rapidly preheated to ~220 °C and then scanned at 5 and 2.5 °C per minute up to 287 °C followed by a 30 minute isothermal hold. Ten runs of oil 7023 sample were made for each scan rate (5 and 2.5 °/minute). The onset of oxidation and the percent residue

results for these tests and the standard deviations are summarized in **Table 9**. The 5 degree/minute scan rate produced the smallest standard deviations in both the oxidation onset temperature and percent residue, although the reduced thermal lag probably produced more accurate onset temperatures at 2.5 °C scan rate.

TABLE 9. STATISTICAL REPEATABILITY OF DSC OXIDATION AND DEPOSITION DATA

SCAN RATE (°C/ MIN)	AVERAGE VALUES + STANDARD DEVIATIONS		
	ONSET OF OXIDATION	% RESIDUE	PEAK WIDTH
2.5*	249.26 \pm 1.84 °C	3.70 \pm 0.6	9
5.0*	258.33 \pm 1.06 °C	4.30 \pm 0.3	11
10.0**	253.8 \pm 4.1 °C	-	-

*1.3 mg, 15 PSI O₂ @ 55 cc/min, C1010 Steel coupon, rapid preheat N₂ to 217 °C, scan to and hold at 287 °C
** 0.7 mg, 15 PSI O₂ @ 55 cc/min, C1010 Steel coupon

4.2.2 APPLICATION/CORRELATION OF THE VOX-DEP RANKING SYSTEM TO 7021-7025 OXIDATION-CORROSION TESTED OILS

The algorithm to calculate the VOX-DEP rating, developed during the first phase of the project, was modified slightly. The volatility onset temperature category was broadened from 3 °C to 5 °C, and provision was made for isothermal bands. The revised algorithm is summarized below in **Table 10**.

TABLE 10. VOX-DEP METHODOLOGY - PHASE II

RELATIVE RANKING ALGORITHM

BEST CATEGORY IS ASSIGNED VALUE 1, NEXT BEST IS 2, ETC

- VOLATILITY ONSET TEMPERATURE:
 - ESTABLISH CATEGORIES SEPARATED BY 5 °C (HIGHEST ONSET IS 1)
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
- OXIDATION ONSET TEMPERATURE METHOD:
 - DSC SCANNING METHOD: ESTABLISH CATEGORIES SEPARATED BY 3 °C (HIGHEST ONSET IS 1)
- DSC ISOTHERMAL METHOD: [DEPENDS ON DELTA TEMPERATURE FROM THE ONSET OF OXIDATION]
FOR 5 °C BELOW OXIDATION ONSET TEMPERATURE, ESTABLISH CATEGORIES SEPARATED BY 1 MINUTE
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
 - OILS WITH AN OXIDATION ONSET TEMPERATURE \leq 220 °C ARE RANKED * (UNACCEPTABLE)
- DEPOSITION DATA:
 - ESTABLISH CATEGORIES SEPARATED BY 3 PERCENT RESIDUE (LOWEST RESIDUE IS 1)
 - OILS WITHIN CATEGORIES ASSIGNED SAME RANKING
- LINEARLY ADD THE RANKINGS
- THE OIL WITH THE LOWEST SCORE IS RANKED FIRST, ETC

The VOX-DEP method was applied to the fresh 7021-7025 oils. The relative ranking of these oils is presented in Table 11. Oils 7023 and 7024 were both ranked 1, followed by Oils 7021 and 7022 which were ranked 2. No weighting factors were used, although they could be. Thus, the excellent oxidative stability and low deposition behavior of oil 7021 was offset by its low volatility temperature. Unfortunately, volatility and deposition measurements were not obtained on the 96 hour samples so an overall VOX-DEP rating could be made. However, the individual VOX-DEP oxidation ratings for the 96 hour oxidation-corrosion samples can be compared to the original fresh oil ratings. The VOX-DEP rating for the oxidation tendency did not generally change as the oils underwent severe stressing during the 96 hour oxidation-corrosion test. Oil 7025 is a special case since it apparently did not contain additives. Oil 7023 did not maintain its original high rating status in the 96 hour test

TABLE 11. VOX-DEP RANKING OF CANDIDATE OILS 7021 THROUGH 7025

MIL-L-7808 SAMPLE DESIGNATION	TIME STRESSED IN OXIDATION- CORROSION TEST	VOLATILITY TENDENCY	OXIDATION TENDENCY	DEPOSITION TENDENCY	OVERALL RANKING
7021	0 hours	4	1	1	2
	96 hours	NOT TESTED	2	NOT TESTED	-
7022	0 hours	3	1	2	2
	96 hours	3	1	NOT TESTED	-
7023	0 hours	2	1	1	1
	96 hours	NOT TESTED	3	NOT TESTED	-
7024	0 hours	1	2	1	1
	96 hours	NOT TESTED	1	NOT TESTED	-
7025	0 hours	2	-	2	-
	96 hours	-	-	NOT TESTED	-
<small>NOTE: RATING 1 IS BEST, 2 IS THE NEXT BEST, ETC. * FAILED MINIMUM VALUE</small>					

series falling all the way to a RR of 3.

Comparison of the VOX-DEP data with the standard viscosity and wear metal for the oxidation-corrosion tested oils was the next step. The viscosity and wear metal data for the fresh and 96 hour samples are summarized in Tables 12 and 13. Close inspection of Table 12 which includes the VOX-DEP oxidation data revealed an interesting correlation. The oxidation onset temperature decreased linearly with viscosity increase for samples 7024, 7021, and 7023. The oxidation onset temperature for the sample 7022, which experienced the largest viscosity increase (15.2 percent), reversed this trend. Its onset decrease of 24 °C was less than of sample 7021 (-29 °C) and sample 7023 (-36 °C) which exhibited 5.7 percent and 9.4 percent viscosity increases, respectively.

TABLE 12. VISCOSITY CHANGES FOR CANDIDATE OILS 7021 THROUGH 7025

SAMPLE DESIGNATION	OXIDATION-CORROSION TEST TIME	VISCOSITY		DSC OXIDATION RESULTS*	
		SUS @ 210 °F	INCREASE	ONSET OXIDATION	TEMPERATURE DECREASE
7021	0 hours 96 hours	72.5 76.6	5.7 %	256 °C 227 °C	29 °
7022	0 hours 96 hours	73.9 85.1	15.2 %	257 °C 233 °C	24 °
7023	0 hours 96 hours	78.6 86.0	9.4 %	255 °C 219 °C	36 °
7024	0 hours 96 hours	84.9 88.8	4.6 %	252 °C 233 °C	19 °
7025	0 hours 96 hours	72.8 too viscous to measure	-	198 °C 240 °C	+42 °

* 0.7 mg sample, 25 PSI O₂ @ 55 cc/min, C1010 Steel coupon, 10°/min

TABLE 13. WEAR METAL ANALYSIS FOR CANDIDATE OILS 7021 THROUGH 7025

MIL-L-7808 SAMPLE DESIGNATION	OXIDATION- CORROSION TEST TIMES	WEAR METALS (ppm)								
		Fe	Cu	Sn	Al	Si	Mg	Zn	Mo	P
7021	0 hours 96 hours	- 2	- -	- -	- -	- 2	- -	- -	- -	3157 3105
7022	0 hours 96 hours	- 2	- -	- -	- -	2 7	- -	- -	- -	818 808
7023	0 hours 96 hours	- 2	- -	- -	- -	4 -	- -	- -	- -	778 795
7024	0 hours 96 hours	- 2	- -	- -	- -	- 2	- -	- -	- -	2517 2510
7025	0 hours 24 hours 64 hours 96 hours	- 1 3 43	- 73 570 5	- 4 6 5	0 0 2 6	1 7 6 55	848 760 2221 442	10 42 442 40	- - - 49	16 7 - 49

These data indicate that once a sample reaches a certain degree of viscosity increase (possibly around 10 percent), the reduction in DSC oxidation onset temperature reaches a maximum. With continued oxidative degradation and viscosity increase, the onset temperature for oxidation will continue to climb until it reaches higher onset temperatures than the original fresh oil. Therefore, oxidation onset temperature and induction times by themselves can be misleading indicators of an oil's stability. Peak shape and breadth as demonstrated in the Phase I Model Oil and additive studies must also be used. The wisdom of using both parameters is dramatically illustrated by the series of DSC oxidation curves for the pure basestock (oil 7025) in Figure 13.

4.3 VOX-DEP ANALYSIS OF J57 ENGINE SIMULATOR TESTED OILS

The ability of the VOX-DEP procedures to predict the relative performance capabilities in actual engines required further correlation and refinement. Although correlations with viscosity and VOX-DEP oxidation ratings could readily be made for the 7021-7025 test series, MIL-SPEC oxidation-corrosion test data do not simulate nor necessarily agree with real engine performance results. Therefore, WRDC/POSL provided three different oils designated A, B and C that were tested for a total of 100 hours in the J57 engine simulator test. Samples were withdrawn at 4 hour intervals. Make-up oil was automatically added after the samples were withdrawn. The engine simulator is described in the AFWAL-TR-82-2123²⁹.

4.3.1 VOX-DEP RESULTS AND DISCUSSION

A summary of the oxidation results and volatility and deposition behavior for the oils stressed in the J57 engine simulator is presented in **Tables 14** and **15**, respectively. The degradation of the oils can be determined from the changes relative to the fresh oil baseline. Scanning DSC oxidation onset results for the fresh oils did not provide a clear oxidative stability differentiation between the oxidative stability of Oils B and C (274 °C and 273 °C, respectively). However, a greater distinction was obtained when isothermal DSC data was evaluated. The resulting induction times revealed that fresh Oils B (9.34 minutes) and C (9.11 minutes) possess nearly equal oxidative stability, exceeding the oxidative stability for Oil A (5.94 minutes) by a large margin. The volatility and deposition data for the fresh oils (**Table 15**) reflect equivalent volatility but different deposition behavior. The smallest to the largest deposit formers were Oils C, B, and A in that order. These data indicate that fresh Oil C would receive the best overall VOX-DEP rating followed in succession by Oil B and Oil A.

Oxidation induction times proved to be even more discriminatory for aged samples, and therefore, were used for the subsequent VOX-DEP analysis. After 100 hours of stressing in the J57 simulator, the DSC induction times for oxidation suggested that Oil C was clearly superior to Oil B as opposed to the equivalency of the fresh oils. The most oxidatively stable oil was Oil C followed by Oil B, and finally Oil A. Interestingly enough, the amount of fresh

TABLE 14. OIL ADDITION EFFECTS ON THE OXIDATIVE STABILITY FOR J57 STRESSED OILS A, B, AND C

OIL A				OIL B				OIL C			
TEST TIME	OXIDATION ONSET *	INDUCTION TIME **	OIL ADDED ***	OXIDATION ONSET *	INDUCTION TIME **	OIL ADDED ***	OXIDATION ONSET *	INDUCTION TIME **	OIL ADDED ***	OIL ADDED ***	
0 HOUR	265 °C	5.94 min	0 ml	274 °C	9.34 min	0 ml	273 °C	9.11 min	0 ml		
40 HOURS	264 °C	4.46 min	4675 ml	269 °C	6.53 min	2125 ml	277 °C	7.63 min	1650 ml		
70 HOURS	266 °C	4.39 min	2805 ml	269 °C	6.42 min	1785 ml	273 °C	7.50 min	1445 ml		
100 HOURS	265 °C	3.22 min	1360 ml	266 °C	5.06 min	1700 ml	276 °C	6.65 min	1360 ml		

TEST CONDITIONS: 15 PSI O₂ @ 55 cc/min, Steel cup

* 2.7 mg, rapid preheat to 220 °C, then 5 °/min
 ** 4.5 mg, rapid preheat to 260 °C, hold isothermally
 *** J57 Engine Simulator Data

TABLE 15. VOX DEP DATA FOR J57 STRESSED OILS A, B, AND C

OIL A			OIL B			OIL C		
TEST TIME	VOLATILITY ONSET *	% DEPOSITION **	VOLATILITY ONSET *	% DEPOSITION **	VOLATILITY ONSET *	% DEPOSITION **		
0 HOUR	182 °C	7.7 %	178 °C	6.4 %	181 °C	5.2 %		
100 HOURS	188 °C	7.5 %	180 °C	9.9 %	210 °C	5.6 %		

TEST CONDITIONS: 15 PSI O₂ @ 55 cc/min, Steel cup

* 0.7 mg, 10 °/min
 ** 4.5 mg, rapid preheat to 217 °C, 5 °C/min to 287 °C, then hold isothermally for 15 min.

make-up oil that was added during the 100 hours test was in reverse order. Oil C had the least amount of make-up oil added (4455 ml), followed by Oil B (5610 ml) and Oil A (8840 ml). These results

indicate that while greater make-up oil is required to offset volatility loss, the replenishment of additional antioxidant does not fully compensate for differences in the thermo-oxidative stability of the original oil formulation. However, the magnitude of the drop (4.28 minutes) for Oil B compared to Oil A (2.72 minutes) suggested that the make-up oil did improve the relative oxidative stability of the remaining aged lubricant. Therefore, a decision was made to explore this additive replenishment effect quantitatively.

Fresh oil additions of various percentages were added to stressed (48 hours in the oxidation-corrosion test) Oil 7021 samples. (Oxidation-Corrosion stressed oil was used since no make-up oil is added during the test.) The additions were representative of make-up oil quantities. Exact antioxidant concentrations of the fresh and stressed oils were determined by the gas chromatographic-mass spectrometry technique. Fresh basestock-additive mixtures were used as calibration standards for the mass spectrometry analysis. Isothermal DSC tests at 230 °C were used to determine the induction time (i.e. oxidative stability) versus antioxidant concentrations for mixtures of 0, 25, 50 75 and 100 percent fresh and aged oils. These results are summarized in **Table 16** and graphically depicted in **Figure 14**.

TABLE 16. OIL ADDITION EFFECTS ON THE OXIDATIVE STABILITY OF OXIDATION-CORROSION STRESSED OIL 7021

PERCENT OF TOTAL VOLUME OF OIL 7021		ISOTHERMAL TEMPERATURE 230 °C	ANTIOXIDANT CONCENTRATION g/Kg of OIL	
48 HOURS	0 HOURS	OXIDATION INDUCTION TIME	[DODPA]	[PANA]
100 %	0 %	2.05 min	2.59 g/Kg	0.18 g/Kg
75 %	25 %	4.01 min	7.74 g/Kg	3.29 g/Kg
50 %	50 %	6.70 min	12.90 g/Kg	6.39 g/Kg
25 %	75 %	9.44 min	18.05 g/Kg	9.49 g/Kg
0 %	100 %	12.80 min	23.20 g/Kg	12.60 g/Kg

2.7 mg, 15 PSI O₂ @ 55 cc/min, C1010 coupon, rapid preheat to 230 °C, hold isothermally

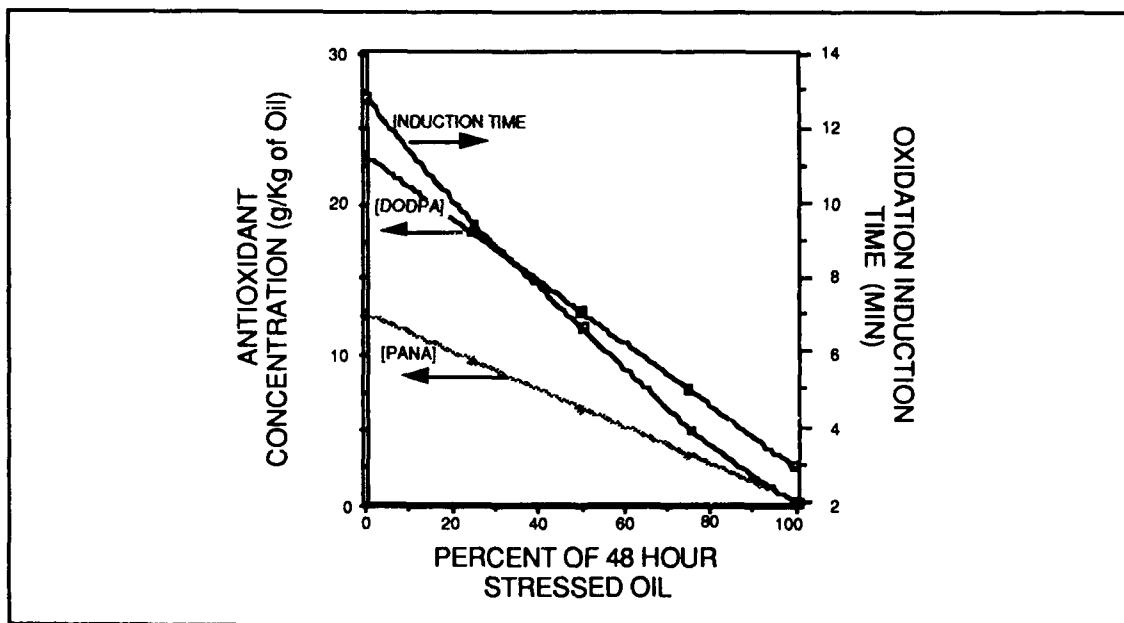


FIGURE 14. FRESH OIL ADDITION EFFECT ON OXIDATIVE STABILITY OF OXIDATION-CORROSION STRESSED OIL 7021

The oil that was stressed for 48 hours (no fresh make-up oil) had a 2.05 minutes DSC induction time and DODPA and PANA concentrations of 2.59 g/kg and 0.18 g/kg, respectively. For the 100 percent fresh oil, the induction time was 12.80 minutes with a DODPA and PANA concentration of 23.2 g/kg and 12.6 g/kg, respectively. As **Figure 14** shows, the effect of antioxidant concentration on DSC oxidation induction time is quite linear. For every 10 percent addition of make-up oil, the induction time increased by approximately one minute, which was equivalent to an increase in antioxidant concentration of approximately 3 grams per kilogram of oil.

Mass spectrometry analysis of the fresh and 48 hour oxidation-corrosion tested oil mixtures also revealed that the depletion rate for PANA is greater than that of DODPA. The difference in the antioxidant depletion rates for DODPA and PANA indicate somewhat different depletion mechanisms³¹. The synergistic nature of these antioxidants (DODPA and PANA) is illustrated by the still appreciable oxidative stability for the 48 hour sample even though only small antioxidant quantities remained in solution³². In summary, these data revealed three key findings:

- (1) There is a direct correlation between the oxidative stability and the antioxidant concentration.
- (2) The DSC (and the VOX-DEP test method) can quantitatively measure the oxidative stability of an oil.
- (3) Make-up oil additions contribute to the maintenance of the oxidative stability of stressed oil.

The quantitative success of the 7021 make-up oil results prompted an analysis of the aged engine simulator oils. The mass spectrometry results for Oil A as it was stressed in the J57 engine simulator tests is depicted in Figure 15. The additive depletion profiles (DODPA, PANA, BTZ and TCP) for Oil A stressed at 0, 20, 40, 60 and 100 hours also reflected the influence of make-up oil additions. Between 40 and 60 hours the additive concentrations remained almost constant, obviously as a result of the 4675 ml of make-up oil that was added after the 40 hour sample was removed (Table 14).

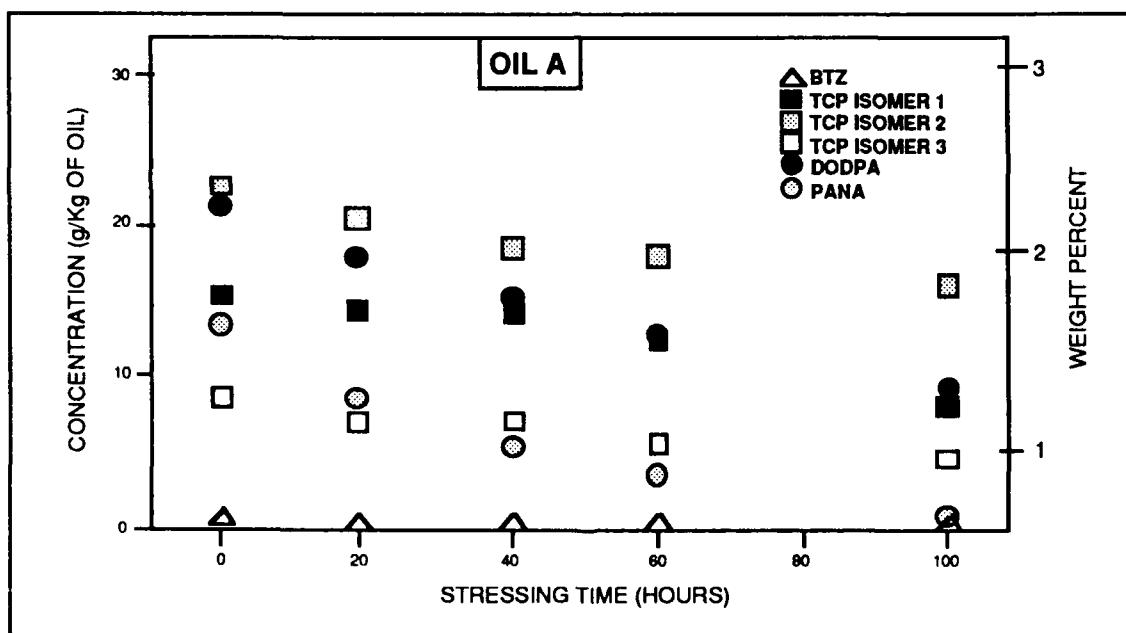


FIGURE 15. ADDITIVE DEPLETION DURING J57 ENGINE SIMULATOR TESTING

The DODPA and PANA antioxidant concentrations and resulting oxidation induction times were plotted as a function of stressing time in the J57 engine simulator. These results are summarized in **Figure 16**. The changes in PANA and DODPA concentrations correlate well with oxidation induction times just as they did in oxidation-corrosion oil 7021 make-up oil tests. Oxidation times stabilized in the 40-70 hour test regime due to the make-up oil. The PANA concentration also remained constant.

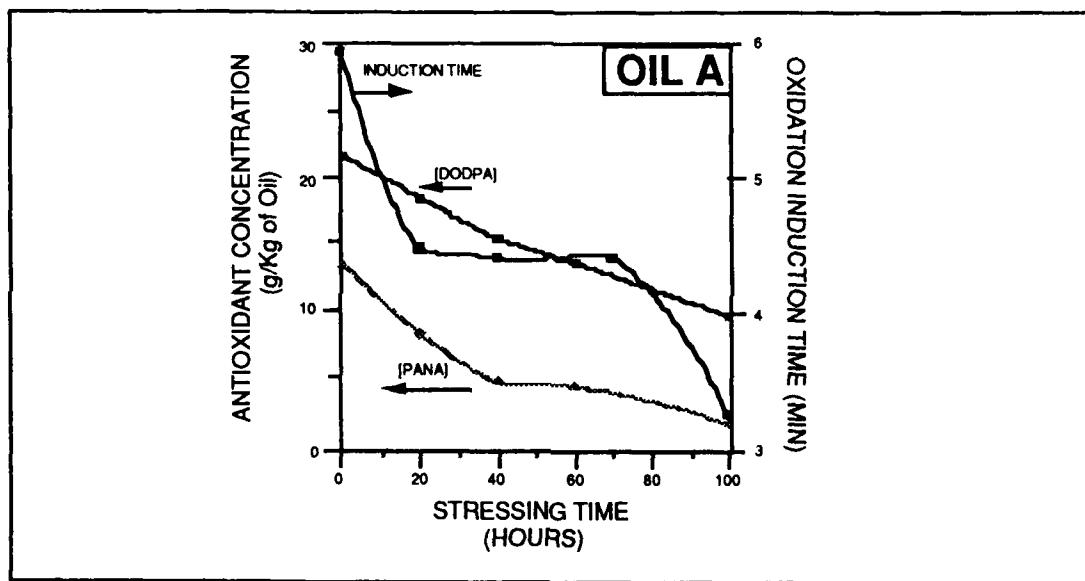


FIGURE 16. OXIDATIVE STABILITY AND ANTIOXIDANT CONCENTRATIONS FOR J57 ENGINE SIMULATOR STRESSED OIL

The dramatic decline in the oxidation induction times after 70 hours correlates with further depletion of the DODPA/PANA concentrations. These data indicate that the critical level of the antioxidant concentration is reached sometime after 70 hours in the engine simulator and that after this time, the oxidation of the oil proceeds

with attendant large increases in T.A.N., viscosity, wear metal concentration and COBRA values (see Table 17). These results are consistent with previous research that found that the antioxidant concentration must fall below a critical antioxidant concentration level of approximately $0.3\text{-}0.4 \times 10^{-3}$ M (molar concentration) before measurable rapid increases in the viscosity, and T.A.N. are observed^{33,34}. The addition of fresh oil prior to reaching the critical effective antioxidant concentration will postpone the detrimental effects of oxidation; after this level is breached, there is little benefit to adding new oil.

TABLE 17. CONVENTIONAL TEST RESULTS FOR J57 STRESSED OILS A, B, AND C

	J57 TEST TIMES	T.A.N. (mg KOH/g of oil)	VISCOSITY AT 40 °C	Fe (ppm)	COBRA
OIL A	0 hours	0.07	12.38	1	5
	40 hours	0.26	12.62	63	12
	70 hours	0.17	12.80	75	12
	100 hours	0.36	13.04	99	19
OIL B	0 hours	0.07	13.50	0	6
	40 hours	0.21	13.96	13	17
	70 hours	0.16	14.22	17	21
	100 hours	0.27	14.62	23	26
OIL C	0 hours	0.07	14.18	0	12
	40 hours	0.02	14.55	12	10
	70 hours	0.04	14.83	19	17
	100 hours	0.18	15.09	32	22

The mass spectrometry results also showed that the existence of three isomeric forms of TCP were depleted at different rates. Most interesting, however, was the linear decrease of isomer 1 and isomer

2 while isomer 3 remained constant after the 40 hour make-up oil addition. The depletion rate of individual TCP isomers and associated antiwear behavior has some interesting practical implications, but is beyond the scope of this program.

4.3.2 APPLICATION AND CORRELATION OF VOX-DEP

The applied VOX-DEP figure of merit rankings for the fresh and 100 hour engine simulator stressed Oils A, B, and C are summarized in **Table 18**. (The underlying data is contained in Tables 14 and 15.) As stated earlier the fresh oil VOX-DEP results indicate that the oils possess equal volatility but different oxidation and deposition characteristics. Fresh Oil A ranked lower than Oil B and Oil C in both oxidative stability and deposit formation tendencies, thereby receiving an overall RR of 3. The better deposition characteristics of fresh Oil C gave it the best overall ranking of 1.

The overall VOX-DEP rankings for 100 hour engine simulator aged samples remained identical to the fresh oil ratings lending credence to the predictability of the VOX-DEP system. However, the order of some individual ratings did change. For example, after 100 hours, Oil C had the poorest volatility ranking and Oil B switched places with Oil A in deposit rankings. In spite of these differences, the overall rankings did not change. Indeed, the dramatic increase in the volatility onset temperature of Oil C as it aged in the Engine Simulator lead to a revision of the VOX-DEP Methodology (**Table 10**) since such an increase is indicative of oil degradation. For an aged oil, an important volatility parameter is the difference between the Volatility Onset Temperature of the stressed oil and the fresh oil; equivalent categories were established based on 5 °C bands. The Volatility Tendency ratings in **Table 18** incorporate that revision.

TABLE 18. VOX-DEP RANKING FOR OILS A, B, AND C

MIL-L-7808 SAMPLE DESIGNATION	TIME STRESSED IN J57 ENGINE SIMULATOR	VOLATILITY TENDENCY	OXIDATION TENDENCY ISOTHERMAL*	DEPOSITION TENDENCY	OVERALL RANKING ISOTHERMAL*
OIL A	0 hours 100 hours	1 2	3 3	3 2	3 3
OIL B	0 hours 100 hours	1 1	1 2	2 3	2 2
OIL C	0 hours 100 hours	1 3	1 1	1 1	1 1

ISOTHERMAL TESTS AT 260 °C

For comparison, the VOX-DEP ratings were compared to conventional oil performance data (such as viscosity, T.A.N., wear metal content and COBRA), which are summarized in Table 17. Oil C displayed the smallest changes in the T.A.N., and COBRA (Complete Oil Breakdown Rate Analyzer) values, and levels slightly above the least viscosity change and lowest wear metal concentrations of Oil A and Oil B, respectively. From the data on make-up oil summarized in Table 14, it is apparent Oil C had the least amount added during the test, followed by Oil B, and then Oil A. Despite the large amount of fresh oil added during the J57 engine simulator test, Oil A still had the greatest change in T.A.N. and the wear metal content. Oil A had almost twice the amount of fresh oil added during the test compared to Oil C, and 80 percent more than Oil B. For that reason, Oil A had the least change in viscosity, followed by Oil C and B in that order. The small amount make-up oil addition and higher viscosity of Oil C

may explain why the volatility temperature of the 100 hour sample is much higher than Oil A and Oil B; i.e., all the light-weight components from the original fresh oil had evaporated. The switch in deposit rating order from 2 to 3 between fresh oil and 100 hour aged Oil B and Oil A samples may also be accounted for by the lower make-up oil additions and larger viscosity increase (8.3% Oil B vs 5.3% Oil A) associated with Oil B. Oil B was intermediate between Oil A and Oil C in T.A.N. increase yet lowest in wear metal concentration. Overall the conventional oil properties data agreed with the VOX-DEP ratings of the fresh and aged oils; i.e., Oil C, Oil B, and Oil A in order of best to worst.

The above applications of VOX-DEP were done comparatively. The VOX-DEP methodology could be developed as an absolute ranking algorithm. In the long run, this absolute ranking approach would be the most desirable. It would require testing of a sufficient number of qualified lubricants, and knowledge of their performance in an actual turbine engine to properly establish the baseline (minimally acceptable) properties, and the width of the equivalent bands.

5.0 SUMMARY OF RESULTS

The following is an overview summary of the key experimental results.

- Volatility onset (stability) is controlled by basestock and not by additive characteristics.
- Oxidation onset is directly influenced by antioxidant concentrations in the Model Oil.
- Scanning DSC oxidation-residue measurements at 5 °C/minute provide high repeatability; however, 2.5 °C/minute test provides greater accuracy.
- DSC oxidation onset temperature decreases with aging until excessive polymerization occurs. Independent viscosity measurements suggest that the oxidation onset temperature decrease reverses direction at viscosity increases of 10 percent and greater.
- A good indicator of degree of aging (polymerization) is the extent of increase in the temperature at which 50 percent weight loss occurs as compared to the fresh oil.
- Isothermal induction times are better discriminators of oxidation stability than scanning onset temperatures for oils of similar stability.
- Direct correlation between antioxidant concentrations and DSC oxidation results via mass spectrometry were achieved, enabling:
 - The effect of aging on the lubricant chemisrty in MIL-SPEC oxidation-corrosion tests to be directly measured; and
 - Make-up oil additions in J57 engine simulator tests to be monitored in terms of additive concentration changes.

6.0 CONCLUSIONS

The critical measure of a laboratory qualification test for jet engine lubricants is its ability to correlate the results to expected performance in operational engines. The characteristics of the VOX-DEP method developed during this project, can be summarized as follows:

- (1) Rapid, easy to use test procedures using readily available commercial equipment;
- (2) Quantitative test results based on fundamental thermodynamic properties;
- (3) Improved insight into T.O.D. degradation mechanisms;
- (4) Correlatability to present MIL-SPEC tests;
- (5) Easy incorporation into present test regimes; and
- (6) Reproducible performance prediction prior and during the course of the laboratory and engine simulator tests.

The VOX-DEP approach aids in predicting the relative performance of oils as they are stressed during the course of a laboratory test or actual engine operation. This investigation successfully demonstrated that VOX-DEP could accurately assess and predict the ultimate relative performance of candidate oils prior to aging in oxidation-corrosion tests and J57 engine simulator operation. VOX-DEP can be applied during the course of the present MIL-SPEC bench tests to provide additional insight into the degradation process that occur throughout the different qualification stressing tests.

The primary distinguishing characteristic of VOX-DEP, compared to other thermal analysis techniques, is that the procedures were carefully developed to optimize correlations with degradation conditions expected in the lubrication system of a jet engine.

The current suite of tests for MIL-L-7808 has evolved over a long period of time, and consequently have a great deal of empirical legacy. But the new lubricants, required for extended service at higher temperatures, have limited duty experience. Therefore, the VOX-DEP procedures can add confidence to predictions of expected lubricant performance based on laboratory tests. The VOX-DEP test procedures would be useful in additive formulations, as well as qualification testing. While the approach used in this investigation compared oils within a test series to each other, they could have been ranked relative to an established standard.

In Conclusion, final recommendations include expanding the VOX-DEP method as follows:

- (1) Incorporate additional features of TGA and DSC data in determining the rankings;
- (2) Use as an additional, complementary MIL-SPEC standard screening test; and
- (3) Apply as an useful lubricant life prediction method by testing aged oil samples from operational fleets.

For the scanning TGA data, the temperature at which 50% weight loss occurs is an additional feature that is useful in judging differences in both fresh and aged oils. The weight loss-temperature slope remains constant over a broad weight loss range around 50% as

opposed to the rapid slope changes that occur around 5% weight loss. Secondly, the 50% weight loss is more characteristic of the bulk lubricant properties rather than the lightest weight components of the lubricant. In addition, the change (increase) in the 50% weight loss temperature of an aged oil sample versus a fresh oil sample is an excellent indicator of the magnitude of an oil's polymerization and viscosity changes. Likewise, the width of the oxidation peak of a fresh oil and its increase as a function of aging is an additional DSC parameter that could be used to compare the oxidation stability of unused lubricants and the remaining useful life of in-service "aged" lubricants, respectively.

Refinement of the VOX-DEP method for incorporation as a MIL-SPEC test would require comparison with standard MIL-SPEC tests on a series of marginal and "good" oils. Lower limits and rating brackets would be set after correlations between the VOX-DEP values and the volatility losses, viscosity and T.A.N. increases and deposit ratings associated with the standard tests are established.

Extensive VOX-DEP characterization of used oils from a variety of operational engines would be compared with other methods (SOAP- COBRA) for predicting remaining useful life. The resultant correlations would result in an additional, and possibly a more precise, method for predicting lubricant condition and its remaining useful life.

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LIST OF ACRONYMS

BTZ	Benzotriazole, a metal passivator additive
COBRA	Complete Oil Breakdown Rate Analyzer
DODPA	Diocetyl diphenylamine, an anti-oxidant
DSC	Differential Scanning Calorimetry
FTMS	Federal Test Method Specification
GC-MS	Gas Chromatograph- Mass Spectrometer
LMW	Low Molecular Weight
MIL-SPEC	Military Specification
PANA	Phenyl-alpha-naphthylamine, an anti-oxidant
PEPA	Pentaerythritol, a basestock of palmitic acid
RR	Relative Ranking
SOAP	Spectrographic Oil Analysis Program
T.A.N.	Total Acid Number
T.O.D.	Thermal Oxidative Deposition
TCP	Tricresyl Phosphate, an antiwear additive
TGA	Thermogravimetric Analysis
TMPTH	Trimethylolpropane ester of heptanoic acid
VOX-DEP	Volatility, Oxidation and Deposition
WRDC	Wright Research and Development Center